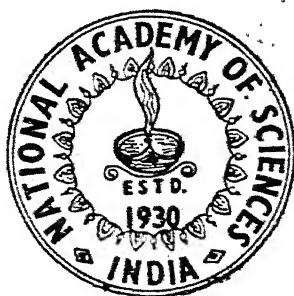


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Part V



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SECTION - A

PART V

THE FALLING CURRENT-POTENTIAL CHARACTERISTIC
UNDER THE SILENT ELECTRIC DISCHARGE :

PART I. THE INFLUENCE OF DIFFERENT DETECTORS.

By

D. P. JATAR and H. D. SHARMA

Department of Physics, University of Saugar

[Received on 12th March, 1959]

ABSTRACT

The paper reports observations of a decrease in current on increasing the applied potential, or a falling current-potential characteristic, in air under the low frequency silent electric discharge using electronic tube detectors, metal rectifiers, crystal diode detectors and the cathode ray oscillograph. The influence of coupling the detector to the L. T. line across a resistance or a transformer is investigated and typical observations of the falling current-potential characteristic in the current picked up by a low capacity frame aerial are also reported. The falling characteristic is observed with all the detectors used except the a. c. microammeter which latter is not sensitive to the higher frequencies present in the discharge current. The results are discussed in the light of the inhibitive influence of the positive ion space charge leading to a preferential suppression of the higher frequency components of the discharge current.

INTRODUCTION

Detailed studies¹ of the variation of the discharge current with the applied potential and the pressure of the gas in hydrogen under the silent electric discharge revealed that over an extended range of pressure and potential the Werner's equation was obeyed.² The equation states³ that the discharge current, i , is a

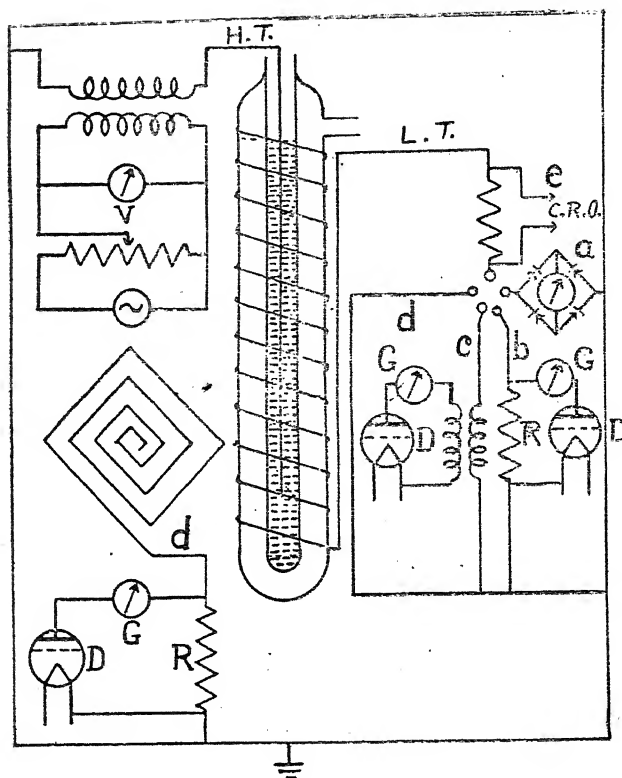


Fig. 1. The general experimental arrangement. V-Voltmeter ; R-Resistance ($6,000\Omega$) ; G-Galvanometer; D-Detector.

The current is measured by (a) a Cambridge double bridge metal oxide rectifier type a. c. microammeter. (b) a detector coupled across the resistance ; (c) the detector coupled across a transformer ; (d) aerial current and (e) a cathode ray oscillograph.

function of both, the applied potential, V , and the overvoltage, $(V - V_m)$, where V_m is the threshold potential. Under simplified assumptions⁴, the equation may be expressed as $V(V - V_m) = B i$, where B depends on the constants of the tube, the pressure of the gas, etc. A similar dependence of i on $(V - V_m)$ for the low frequency silent electric discharge has been pointed out by Joshi⁵. However, under certain conditions especially at low pressures it was observed¹ that i decreased with increasing V over a certain range, i. e., a falling or negative current-potential characteristic was observed. Essentially similar results were also obtained in air⁶. Investigations of the influence of a. c. supply and the mode of coupling the detector to the L. T. line, on the falling characteristic in hydrogen indicated⁷ that the inhibitive influence of the positive ion space charge leading to a preferential suppression of the higher frequency components of the discharge current may be responsible for the phenomenon. It was therefore of interest to investigate in detail the influence of different parameters on the falling characteristic to elucidate its mechanism. The present paper reports the influence of the detectors on the falling characteristic.

EXPERIMENTAL

The general experimental arrangement was essentially similar to that employed earlier and is shown in Fig. 1. Laboratory air filtered through glass wool and dried finally over P_2O_5 was used. The discharge tubes used were all glass ozonisers of the Siemens type, and were excited by an H. T. transformer using 50 c/s. a. c. The following methods were adopted to measure the current flowing through the discharge tube; In (a) fig. 1, a Cambridge double bridge metal oxide rectifier type a. c. microammeter was used. In (b), the current was measured by a moving coil galvanometer, G , in the plate circuit of a detector, D , connected to the L. T. line across a resistance, R . The following detectors were used: (i) a germanium crystal diode (1N34); a Westector type metal rectifier, and (iii) electronic tubes (RCA 30, 1H5GT, 1H4G, and DAC32). In (c) fig. 1, the detector was connected to the L. T. line across an audio frequency transformer (Ratio 1:2). To measure the aerial current, the L. T. line was earthed directly (in (d) fig. 1) and the current was picked up by a low capacity frame aerial, kept at a distance of approximately 10 cm. from the tube, and measured by the galvanometer in the plate circuit of the detector connected across a resistance. The waveform of the discharge current was also investigated simultaneously by feeding the potential drop across another serial resistance to the vertical input of the cathode ray oscillograph (fig. 1 e). All these observations* were taken with the tube in dark to avoid the change in current due to the influence of even visible light.

RESULTS

As the potential applied to the tube is increased from zero, no current is registered till a critical potential is reached at which there is a sudden rise in the current flowing through the tube and a glow characteristic of the gas in the tube sets in. This is accompanied by the appearance of pulses on the current oscillogram. This critical potential is called the threshold potential, V_m . The potential beyond this was increased in regular steps and the corresponding values of the current were noted.

Grateful thanks of the authors are due to Professor S. S. Joshi of the Banaras Hindu University for the loan of the a. c. microammeter, the germanium crystal diode (1N34) and the Westector detector which made this study possible.

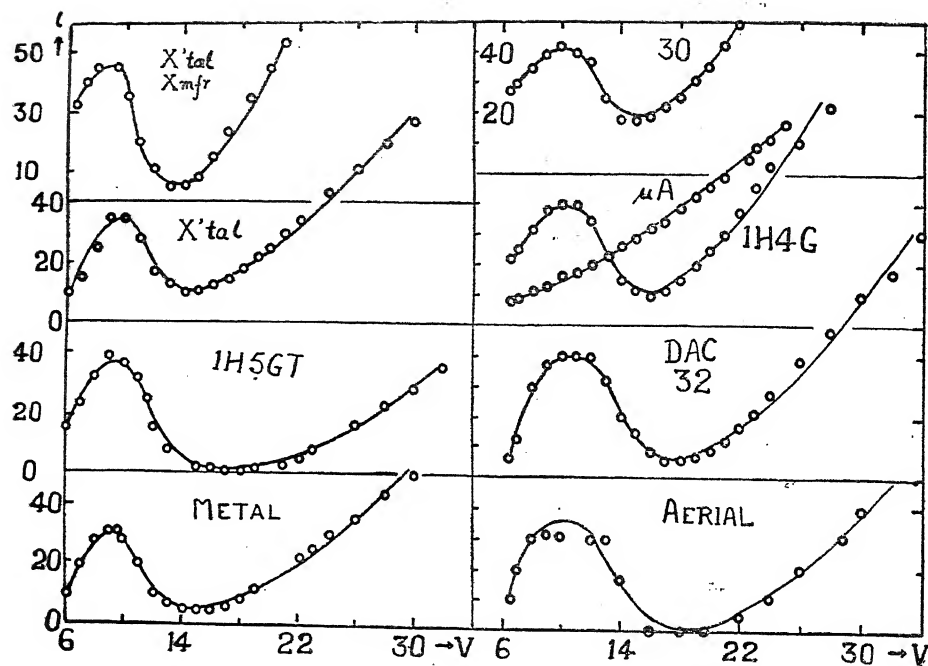


Fig. 2. Variation of the discharge current, i , with the applied potential, V , using different detectors. i in arbitrary units; V in volts rms (primary), (transformer ratio 20,000/230).

X'tal Xmf'r-germanium crystal diode (1N34) coupled across the transformer; μ A-Cambridge a. c. microammeter. For the remaining curves detector coupled across resistance. X'tal-1N34; Metal-Wetector type metal rectifier; Electronic tubes 1H5GT, 1H4G, RCA30 and DAC32; Aerial-Aerial current using 1N34 and a more sensitive galvanometer.

Typical results only for one tube filled with air at 1 mm. Hg. are shown in fig. 2. It is seen that in all cases, except when the a. c. microammeter is used, a falling current-potential characteristic is observed, i. e., as the potential is increased gradually above V_m , the current initially increases to a maximum after which it diminishes to a minimum value while the potential is increasing, and then finally increases continuously. With the various modes of current detection employed, the potential for the initial maximum and that for the minimum in current do not appear to be appreciably altered. With the microammeter, however, the current increases continuously as the potential is increased and the falling characteristic is not observed.

Oscillograms of the discharge current are shown in fig. 3. It is seen that the amplitude of the pulses, which appear at V_m initially increases slightly as the potential is increased gradually and then begins to diminish and the trace becomes pulse-free. The potential at which the diminution in the amplitude of the pulses commences corresponds closely with the potential at which the diminution in current is registered. At still higher potentials, some pulses reappear and their number increases with the applied potential, corresponding to the increasing current. In the region corresponding to the minimum current, the current trace is observed to be pulse-free. It is of interest to note that the current picked up by the frame aerial remains zero over the potential range for which the current trace is pulse-free. The amplitude of the sinewave, on the other hand, increases continuously with the applied potential.

DISCUSSION

The falling current-potential characteristic in d. c. discharges using metal electrodes has been investigated by a number of workers and different mechanisms have been proposed to explain it. These have been discussed recently to explain the falling characteristic in hydrogen under the low frequency silent electric discharge⁷. To explain the marked falling characteristic in poorly ventilated or moist air at atmospheric pressure under positive corona, Fitzsimmons⁸ states that the abnormally rapid space charge fouling leads to a drop in current until the potential is raised to a value where the applied fields can clear the space charge. The falling characteristic for corona discharges between coaxial cylinders has also been ascribed by Druyvesteyn and Penning⁹ to the positive space charge. It is not unlikely that the falling characteristic observed in the present case is also due to an increase in the positive ion space charge.

Studies^{1,10} of the discharge current and the Joshi effect in hydrogen in these laboratories revealed three distinct regions in the current potential characteristic corresponding to the initial fast rise, the intermediate sag region and the final fast rise in the conductivity. From these it was suggested^{1,4,10} that the three regions correspond to the space charge free, the space charge limited and the steady corona regimes. Thus in the intermediate sag region, space charges increase the corona gap resistance and tend to choke off the discharge pulses. This was supported by the oscillographic studies of the discharge current which showed that in the intermediate sag region the amplitude of the pulses on the 50 c/s. current trace decreased slightly as the potential was increased while the base 50 c/s. trace increased. Such a choking action of the positive ion space charge in point to plane and coaxial cylinder coronas is well known². Thus in the intermediate sag region, as the potential is increased the current measured by a current detector should diminish due to the decrease in the amplitude of the pulses. On the other hand, the current should increase due to the increase of the 50 c/s. supply frequency component.

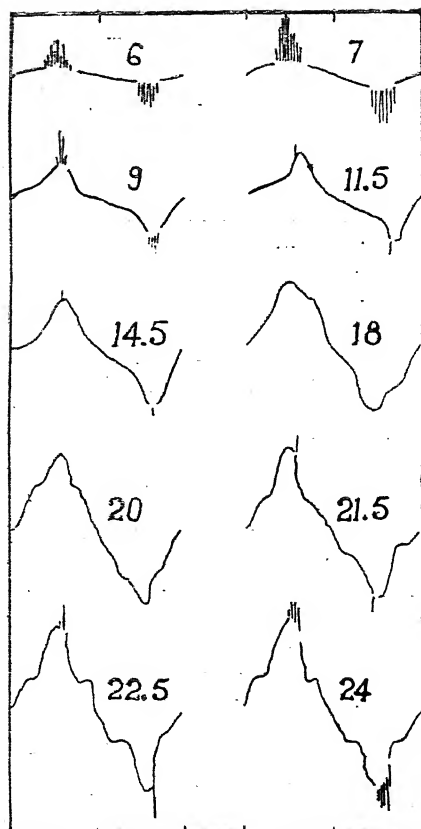


Fig. 3. Oscillograms of the discharge current. Numbers on traces indicate the applied potential in volts rms (primary).

For the detectors which are sensitive to the higher frequency components also, when the rate of decrease of current due to the pulses is faster than its rate of increase due to the supply frequency component, the characteristic should become negative or falling. The results reported here are in accord with this.

The observation of the falling current-potential characteristic using different detectors and the close agreement for the different detectors in the potential for the initial maximum and in that for the minimum current, are to be anticipated on the above view. The a. c. microammeter is, however, not sensitive to the higher frequency components. The absence of the falling characteristic with the microammeter and a continuous increase of current with the applied potential are in accord with this. This is further borne out by the observation that while the other detectors register a sudden increase in current at V_m due to the appearance of the pulses, no such large change is perceptible in the microammeter. It is significant to note here that the current picked up by the aerial is entirely of higher frequencies, 50 c/s. being absent. It is to be anticipated therefore, that over the potential range where the higher frequency pulses are not present as seen on the oscillograph, the current registered in the aerial pick up should be zero, as actually observed. Joshi has shown¹¹ that the higher frequency pulses are preferentially damped by a high resistance in the L. T. line. Use of a high coupling resistance should therefore diminish the current due to the pulses. The appreciably faster rise when the detector is coupled across a transformer may be attributed to this. This is further borne out by studies of the influence of coupling resistance on the falling characteristic, to be reported elsewhere.

The authors wish to thank Professor S. S. Joshi of the Banaras Hindu University for his keen interest and helpful criticism.

REFERENCES

1. D. P. Jatar, *Journ. Univ. Saugar*, 6 (II) A, 60 (1957).
2. D. P. Jatar, *Journ. Chem. Phys.*, 24, 1273 (1956).
3. L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases*, John Wiley and Sons, New York (1939).
4. D. P. Jatar, *Canadian Journ. Phys.*, 36, 1551 (1958) ; See also Ref. 2.
5. S. S. Joshi, *Trans. Farad. Soc.*, 25, 118 (1929).
6. D. P. Jatar and H. D. Sharma, *Sci. and Cult.*, 23, 43 (1957-58).
7. D. P. Jatar, *Journ. Sci. Res. Banaras Hindu Univ.*, (in press).
8. Fitzsimmons, *Phys. Rev.*, 61, 175 (1942).
9. M. J. Druyvesteyn and F. M. Penning, *Rev. Mod. Phys.*, 12, 87 (1940).
10. D. P. Jatar, *Nuovo Cimento*, 8, 290 (1958).
11. S. S. Joshi, *Proc. Ind. Acad. Sci.*, 22A, 225 (1945).

THE REDUCTION OF PERMANGANATE AND MANGANESE DIOXIDE BY MALIC ACID

By

YUGUL KISHORE GUPTA and RUP DUTTA

Chemical Laboratories, D. A. V. College, Kanpur

[Received on July 18, 1959]

ABSTRACT

The reduction of permanganate by malic acid is attended with small induction period, which increases in presence of sulphuric acid, but decreases with the increase in the concentration of malic acid. Vanadium sulphate has pronounced catalytic effect. Manganous ion acts as a catalyst in the beginning, but retards the rate towards the end of reaction. Reduction of manganese dioxide by malic acid has also been studied to confirm the anticatalytic action of Mn (II). Entropy of activation has been calculated for the slow reduction of Mn (III) complex.

Sanyal and Dhar¹ reported the oxidation of malic acid by permanganate to be an induced reaction. Hatcher and West² studied the oxidation to know the oxidation stages of malic acid. Systematic study of the reduction of permanganate by malic acid has not been made so far. We have carried out the reduction following the kinetics iodometrically. Reduction of permanganate from Mn (VII) to Mn (II) is said to occur step by step and Mn (IV) and Mn (III) are the only intermediate states which are stable in acid medium. The reduction of MnO_2 by malic acid was also studied because MnO_2 on reduction gives Mn (III) which forms complex with malate, similar in colour and composition to the one obtained by the reduction of permanganate. The reduction of MnO_2 by oxalate has already been studied by Ghosh and coworkers^{3,4}.

EXPERIMENTAL

Stock solutions of B.D.H., A.R. potassium permanganate and Riedel malic acid were prepared in the redistilled water. All other chemicals used were either of B. D. H., A. R or E. Merck quality.

The reaction was studied in a thermostat at 25° C. 5 ml. of the reaction mixture were taken out from the reaction vessel at suitable intervals of time and added to an acidified solution of 7% KI. The liberated iodine was titrated against 0.005 N sodium thiosulphate. Malic acid did not react with iodine within the time for which the titration was done.

Suspension of manganese dioxide was obtained by mixing permanganate with an excess of manganous sulphate in presence of potassium sulphate. It was thoroughly washed several times with distilled water to free it of sulphate ions. The suspension was well shaken before taking any samples. Its oxidising capacity was determined iodometrically. A preliminary study indicated that manganese dioxide does not dissolve as quickly as oxalate⁴. The reaction vessel was continuously shaken by an electric shaker to check the manganese dioxide particles from settling to the bottom till the reaction mixture became transparent after about 8 to 10 minutes.

RESULTS AND DISCUSSION

Oxidation of malic acid is much faster than that of malonic acid⁵ though not as fast as oxalate^{3,4}. Results with permanganate are shown in figures from 1 to 4 where oxidant concentration in ml. of 0.005 N $\text{Na}_2\text{S}_2\text{O}_8$, has been plotted against time. The $-d(\text{oxidant})/dt$ curves are slightly different than those in case of oxalate or malonate. The reaction has a slight induction period followed by the quick fall in the oxidant concentration. Fig. 1 shows the effect of changing the concentration of malic acid. The induction period completely disappears with higher concentrations of malic acid (cf. oxidation of oxalate⁵) and there is an overall increase in the rate. No change in the rate was observed by varying the concentration of permanganate and hence these results have not been shown.

From fig. 3 it may be seen that the induction period increases with the increase in the concentration of sulphuric acid. Cabellow and Garcia⁷ and Cabrera and Rio⁸ have also reported the same behaviour of the mineral acids in the oxidations of tartaric and citric acids respectively. It may be seen that the acid, though retarding the reaction in the initial stages, enhances the rate towards the end. Thus as a whole there is an overall increase in the rate of the reaction in presence of sulphuric acid. We did not observe any increase in the induction period by increasing the concentration of malic acid i.e., decreasing the pH. It appears that the effect of increased concentration of malic acid is much more than the effect of decreasing the pH.

The catalytic effect of manganous sulphate is large as may be seen from fig. 2. Mn (II) is well known to act as an anticatalyst towards the end of almost all reductions of permanganate. In the present case the anticatalytic effect is masked by the catalysing influence of hydrogen ions. However, from fig. 2 it is clear that the curves for manganous sulphate have a tendency to decrease the rate towards the end. Vanadium sulphate increases the rate to a great extent.

REACTION WITH MnO_2

It is known that the reduction of permanganate takes place in several steps through the formation of Mn (IV) and Mn (III) and that the slow reduction of permanganate towards the end is that of Mn (III). Manganese dioxide on reduction gives Mn (III) and the former was used to confirm the anticatalytic effect of Mn (II). All experiments with MnO_2 upto the interval of 5 to 7 minutes may be complicated due to the dissolution of MnO_2 by malic acid, but thereafter they represent the reduction of yellow malate complex of Mn (III).

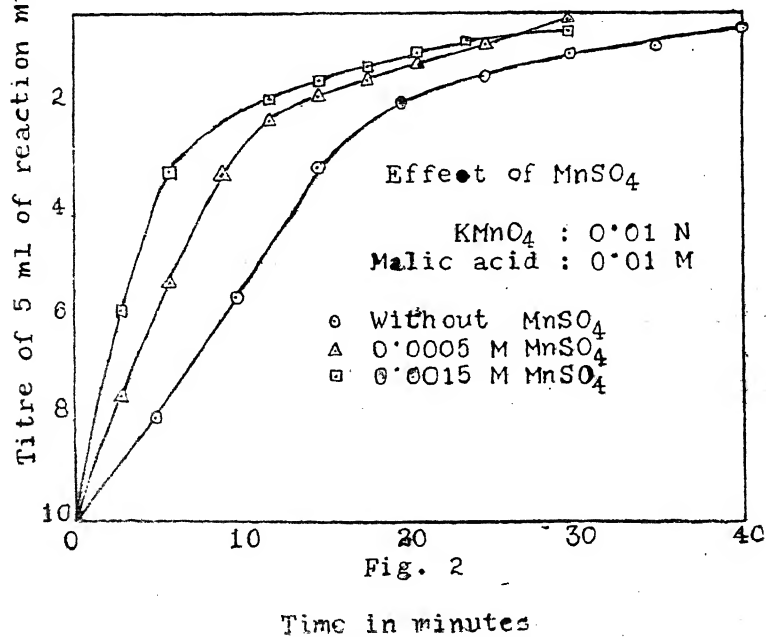
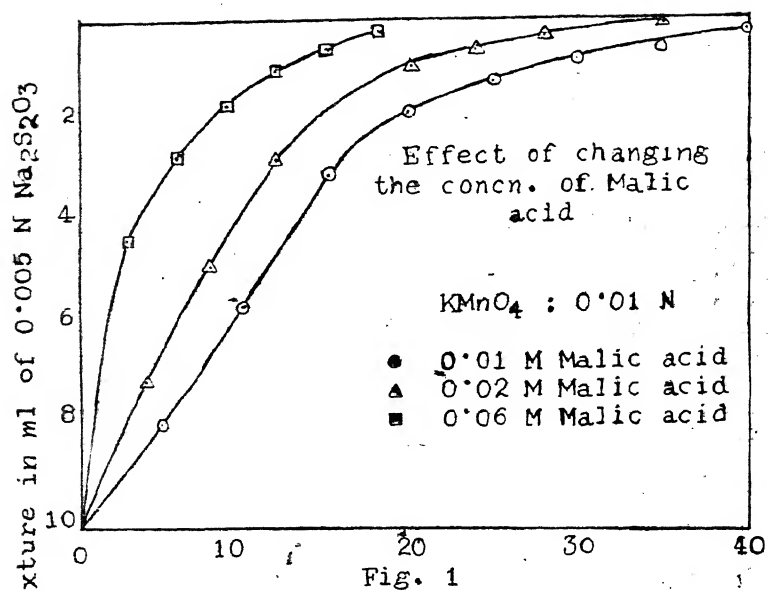
The slow decomposition of the complex is found to be first order in Mn (III) and the constants have been calculated from the relation

$$k = 2.303/t \times \log a / (a - x)$$

where a and $a - x$ are the concentrations of the oxidant initially and after time t . Figs. 5 and 6 give the plot of $\log a / (a - x)$ against time wherein straight lines are obtained.

Fig. 5 shows the effect of changing the concentration of malic acid. It would appear that the rate increases with the increase in the concentration of the acid. The order calculated by Vant Hoff's method, is 0.3. We are of the opinion that the increase in the rate is due to decrease in the pH and the concentration of malate ion has little effect.

Reduction of KMnO_4 by Malic acid



Results with manganous sulphate and sulphuric acid have been shown in fig. 6. Sulphuric acid catalyses and manganous sulphate retards the reaction. This confirms the anticatalytic effect of Mn (II) towards the end of reduction of permanganate by malic acid. Potassium sulphate and nitrate lower the rate. The average velocity constants in presence of these substances have been shown in table 1.

TABLE 1
Malic acid: 0.4M; MnO₂: 0.01 N

Electrolyte	Concentration	$k \times 10^3/\text{min.}$
—	—	6.18
H ₂ SO ₄	0.1 M	8.93
H ₂ SO ₄	0.05 M	7.59
MnSO ₄	0.10 M	4.14
MnSO ₄	0.05 M	4.93
K ₂ SO ₄	0.25 M	5.01
KNO ₃	0.25 M	5.23

ENERGY AND ENTROPY OF ACTIVATION

The reaction was studied at 35°C and the average k was $13.71 \times 10^{-2} \text{ min.}^{-1}$. The energy of activation calculated from the Arrhenius equation, was found to be 14480 cal. Frequency factor, A and entropy of activation, Δs ; were calculated from the following relations:

$$\log k = A - E/2.303RT \quad \text{and}$$

$$k = (KT/h) \times e^{\Delta s/R} \times e^{-\Delta H/RT}$$

where 'K' and 'h' are Boltzman's and Planck's constants and ΔH is not much different than 'E'. A and Δs were found to be $4.86 \times 10^7 \text{ sec.}^{-1}$ and -24.31 E. U. respectively.

Reduction of permanganate is complicated by the occurrence of several steps of different rates of reaction. The reduction occurs from Mn (VII) to Mn (II) state. The reaction is slow at two stages, in the beginning and towards the end. It is well known that the reaction towards the end is the slow reduction of trivalent manganese complex. Hence the slow step in the beginning must be due to a step being slow in the reduction of permanganate from Mn (VII) to Mn (III). Reduction from Mn (VI) to Mn (V) or from Mn (V) to Mn (IV) are believed to be very fast as these states are very unstable in acid medium. Reduction of Mn (IV) to Mn (III) is also quite fast as we have already seen. Hence it is concluded that the induction period is due to the slow reduction of Mn (VII) to Mn (VI) state. Mn (II) has been found to be a good catalyst and no induction period is observed in that case. Hence in other words, it may be said that the induction period is due to want of manganous ions. As soon as a suitable concentration of Mn (II) is obtained from permanganate

Reduction of KMnO_4 by Malic acid

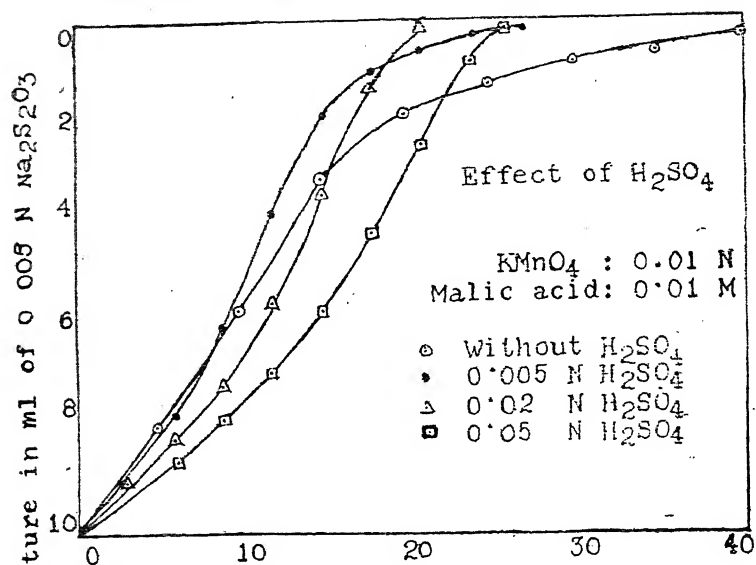


Fig. 3

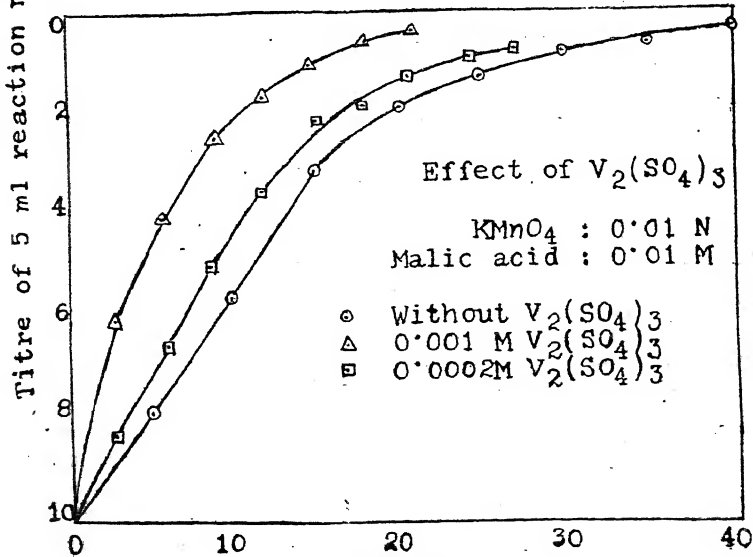
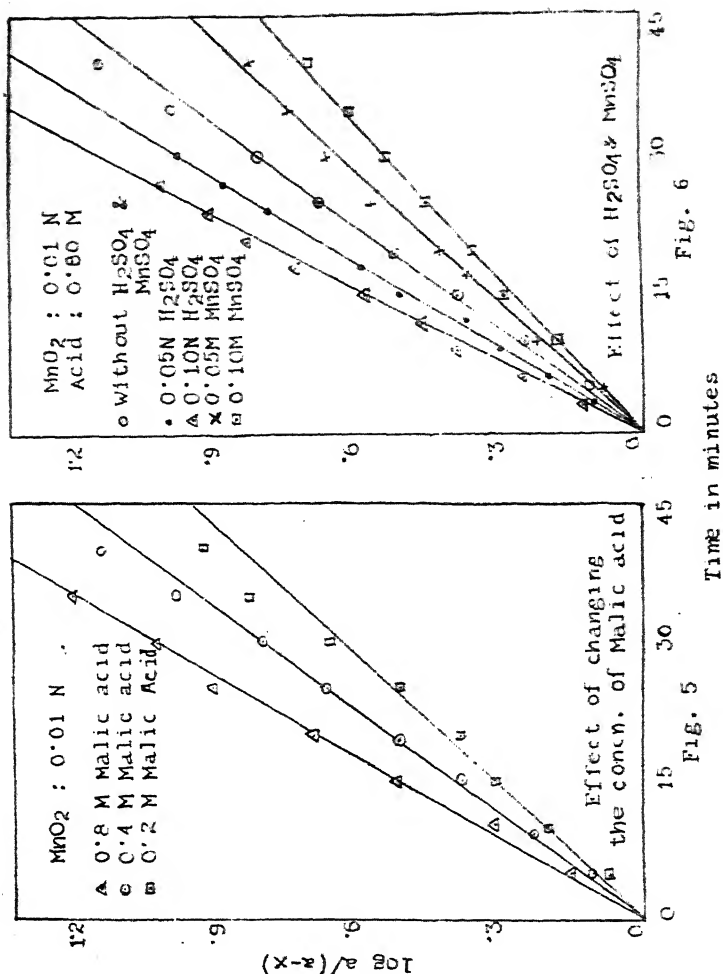


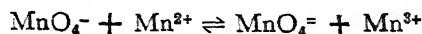
Fig. 4

Time in minutes

Reduction of MnO₂ by Malic acid

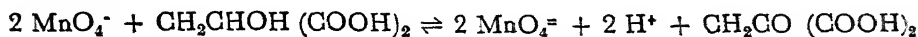


by gradual reduction, it directly reacts with the permanganate according to the following mechanism suggested by Polissar⁹, and Gupta and Ghosh¹⁰ :—



MnO₄^{·-} soon disproportionates into MnO₂ which also quickly dissolves in the organic acid and thus the steep portion of the 'S' shaped curve is characteristic of this series of fast reactions.

The reduction of permanganate in the initial stages, depends on the concentration of malic acid and is retarded by hydrogen ions, perhaps according to the following step :—



It may, however, be stated that Hatcher and West⁸ have excluded the possibility of the formation of oxalacetic acid as the intermediate in the oxidation of malic acid. In fact not much is known about the oxidation stages of malic acid.

In many other permanganate reductions, the first step is sufficiently slow which results in large induction periods. In the present case, this step is not very slow and hence large induction periods are not observed.

Malate complex of Mn (III) have not been reported so far, but there is little doubt that the yellow coloured solution obtained by the reduction of MnO_2 is nothing else but this malate complex. The reduction of this complex is first order in Mn (III) and does not depend on the concentration of malic acid. It is anticatalysed by the manganous ions. It appears that the step



which has been suggested by Ghosh and coworkers^{8,10} for the oxidation of oxalate, occurs in the present oxidation also. Anticatalytic action of H^+ on this step is not observed because its catalytic activity on the dissolution of MnO_2 and other intermediate steps, is much great. The entropy of activation is negative as compared to the normal value of -4 E. U. for unimolecular reaction, which suggests the reaction between similarly charged ions or between a charged ion and a neutral molecule. The rate slightly decreases in presence of potassium sulphate and potassium nitrate. This may suggest a reaction between oppositely charged ions or between an ion and a neutral molecule. These conclusions support the above step of reduction of Mn (III).

REFERENCES

1. Sanyal, R. P. and Dhar, N. R., 1924, *Z. anorg. Chem.*, **134**, 161.
2. Hatcher, W. H. and West, C. R., 1927, *Trans. Roy. Soc., Canada*, **21**, 269.
3. Chakravarti, D. N. and Ghosh, S., 1957, *Z. physik. Chem.*, **207**, 392.
4. Gupta, Y. K. and Ghosh, S., 1958, *Z. physik. Chem.*, **208**, 368.
5. Gupta, Y. K. and Dutta, R., Unpublished work.
6. Gupta, Y. K. and Ghosh, S., 1958, *Z. physik. Chem.*, **209**, 310.
7. Cabellow, A. S. and Garcia, H. S., 1952, *Anales real Soc. espan fis. y quim (Madrid)*, **48B**, 281.
8. Cabrera, L. and Rio, G. Del, 1953, *Ibid.*, **49B**, 263.
9. Polissar, M. J., 1936, *J. Am. Chem Soc.*, **58**, 1372.
10. Gupta, Y. K. and Ghosh, S., 1959, *Z. physik. Chem.*, **210**, 1.

CHEMICAL EXAMINATION OF SEEDS OF PHASEOLUS GLABRA—PART III

STUDIES ON STEROL

By

A. SINHA

Chemical Laboratory, Medical College, Agra

[Received on 23rd Sept., 1959]

ABSTRACT

β -sitosterol has been isolated from the oil of *Phaseolus Glabra*. Physical and chemical properties of the sterol have been studied and its digitonide, acetate, benzoate, acetate bromide and dinitrobenzoate prepared and compared with the authentic samples.

Phaseolus Glabra (N. O. Papilionaceae) is a perennial climbing plant, grown extensively in India. The green pods are used as vegetables and ripe large seeds are eaten boiled whole with condiments. The seeds contain large amounts of proteins and are claimed to have aperient properties. The studies on the oil¹ and on mucilage² obtained from the seeds have earlier been described by the author. The present investigation reveals that oil from the seeds of *Phaseolus Glabra* contains 2.35% of unsaponifiable matter. From this unsaponifiable matter, a crude sterol has been obtained. On purification, it yielded 56.2% sterol and 43.8% a gummy semi-solid residue. Pure sterol has been isolated from this fraction by repeated crystallisation of the corresponding acetate and benzoate and by chromatography over alumina. The sterol on crystallisation according to the technique adopted by Anderson³ showed no alteration in specific rotation. Its molecular formulae has been found to be $C_{29}H_{50}O$. The melting points and rotational values correspond to those of β -sitosterol⁴. It has been found to contain one double bond and one hydroxyl group. The characteristics of the sterol have further been confirmed by the preparation of digitonilide m. p. 230° (decomp.) and liberation of the original sterol showing the presence of 3- β -hydroxyl group in the molecule. Melting points (uncorrected) were taken on Kofler block and rotations were measured in chloroform solutions (conc. 1%).

EXPERIMENTAL

The seeds required for the present investigation were collected from the local area and after being allowed to dry in sun were stored in a dry place. The dried seeds were crushed, shell removed and after being ground, was subjected to soxhlet extraction with petroleum ether (b. p. 40°–60°). The oil obtained, after removal of petroleum ether in 5.0% yield was redish brown in colour.

Isolation of sterol :—The oil (1 Kg.) was hydrolysed by refluxing on a water bath for 12 hours with a large excess of 20% alcoholic potassium hydroxide. After hydrolysis, the product was diluted with a little water and the alcohol was evaporated off on a water bath with the addition of a corresponding amount of water from time to time. The alcohol-free alkaline solution was extracted several times with petroleum ether (b. p. 40–60°) in an all glass soxhlet. The extract was

washed with water, dried over fused CaCl_2 and the solvent distilled when the crude sterol fraction was obtained. This product was dissolved in methyl alcohol and kept at 0° for 18 hours when the precipitate of the sterol (56.2%) and a gummy semi-solid residue (43.8%) were obtained. The crude sterol fraction was completely dried in a vacuum desiccator.

Purification of sterol :—The crude sterol fraction was purified by chromatography of the product over Brockmann aluminium oxide using petroleum ether (b. p. $40^\circ - 60^\circ$) and benzene and chloroform (3:2, v/v) successively as eluents. The benzene-chloroform fraction was found to contain the sterol in the form of shining flakes. The product was recrystallised several times from ether-alcohol mixture (1:1, v/v) and finally crystallised from methyl alcohol when shining flakes, m. p. 136° , $[\alpha]^{25}_D = 37^\circ.0$ (CHCl_3) were obtained. (Lit. m. p. $136^\circ.5 - 37^\circ.5$, $[\alpha]^{25}_D = 36^\circ.6$). The petroleum ether fraction, consisted of a waxy material melting indefinitely from $50^\circ - 60^\circ$. The sterol was freely soluble in benzene, chloroform and petroleum ether and sparingly soluble in cold methyl and ethyl alcohol. The sterol gave positive Salkowski reaction and in the Libermann Burchard reaction, it assumed a pink changing to blue and then green colouration. In the Steine-Khlenberg reaction, a purple colouration was observed, which on exposure to light turned cobalt blue. (Found: C, 84.00; H, 11.96; Mol. Wt. 421. $\text{C}_{29}\text{H}_{50}\text{O}$ requires C, 83.98; H, 12.15%).

Preparation of sterol acetate :—The sterol (0.5 g.) was heated under reflux with 2.5 c. c. of acetic anhydride at 140° for 2 hours in an oil bath. The reaction product was cooled and filtered from the separated plates which were dried over fused CaCl_2 in a vacuum desiccator. The sterol acetate was crystallised from methyl alcohol in colourless needles, m. p. 126° , $[\alpha]^{25}_D = 41^\circ.5$ (Lit. m. p. $126^\circ - 27^\circ$, $[\alpha]^{25}_D = 42^\circ$), yield 80.5%. (Found: C, 81.49, H, 11.36%. $\text{C}_{31}\text{H}_{52}\text{O}_2$ requires C, 81.57, H, 11.47%).

Hydrolysis of sterol acetate :—Sterol acetate (0.1 g.) was hydrolysed with 5 c. c. of absolute alcohol, 0.5 g. potassium hydroxide and 0.5 c. c. water by heating on a water bath under reflux for 6 hours. After the hydrolysis, alcohol was removed, the residue diluted with water and was extracted with ether. On removal of ether, the sterol was crystallised from absolute alcohol in shining flakes, m. p. $136^\circ.5$, $[\alpha]^{25}_D = 36^\circ.0$ (CHCl_3). (Found: C, 84.0; H, 11.98%. Mol. Wt. 419. $\text{C}_{29}\text{H}_{50}\text{O}$ requires, C, 83.98; H, 12.15%).

Preparation of sterol benzoate :—Benzoyl chloride (0.25 c. c.) was added to an ice-cold solution of the sterol (0.1 g.) in pyridine (2.0 c. c.) and 0.2 c. c. methyl alcohol. The mixture was kept at 20° for 16 hours, decomposed by addition of crushed ice, acidified with conc. hydrochloric acid and extracted with ether. The ethereal extract was washed successively with dil. HCl , sodium bicarbonate solution, water and then dried over fused CaCl_2 . On removal of ether the sterol benzoate was crystallised from a mixture of ethanol-ether in clusters, m. p. 144° , $[\alpha]^{25}_D = 14^\circ.5$ (CHCl_3). (Lit. m. p. $144^\circ - 145^\circ$, $[\alpha]^{25}_D = 14^\circ$). Found: C, 83.29; H, 10.43%. $\text{C}_{36}\text{H}_{54}\text{O}_2$ requires, C, 83.34; H, 10.49%.

Preparation of sterol acetate bromide :—The sterol acetate was brominated by the method of Windaus and Hauth⁵ and was obtained as a pale yellow amorphous powder, m. p. 115° . Found: Br, 25.80%. $\text{C}_{31}\text{H}_{52}\text{O}_2\text{Br}_2$ requires Br, 25.97%.

Preparation of sterol digitonide :—The sterol digitonide was prepared by the method of Bhargava and Singh⁶ and was obtained as a white flocculent powder,

m. p. 230 (decomp.). Found: C, 61.83; H, 8.5%. $C_{27}H_{46}O$ C, $H_{46}O_{1.9}$ requires C, 61.91; H, 8.6%.

Preparation of sterol di-nitrobenzoate :—3:5 di-nitro-benzoate derivative of the product was prepared as usual and recrystallised from a mixture of ethyl acetate and petroleum ether (b. p. 40° - 60°) and finally from a mixture of methanol and chloroform, when it melted at 200° (Lit. m. p. 202° - 203°).

Identification of the sterol :—From a comparison of the analyses, melting points and rotation of the sterol, the acetate and benzoate, with those for known sterols, the sterol was identified as β -sitosterol. The results are also in conformity with the results reported earlier by the author⁷ in the case of sterol from *Pongamia Glabra*, Vent (N. O. Papilionaceae).

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REFERENCES

1. Sinha, A., *Indian J. Appl. Chem.*, **22**, 31 (1959).
2. Sinha, A., Communicated. *ibid.*,
3. Anderson, *J. Amer. Chem. Soc.*, **48**, 2975, 2987 (1926).
4. Wallis, et. al., *J. Org. Chem.*, **2**, 336, 341 (1938).
5. Windaus and Hauth, *Ber.*, **39**, 4378 (1906).
6. Bhargava and Singh, *J. Indian Chem. Soc.*, **35**, 763 (1958).
7. Sinha, A., *Indian J. Appl. Chem.*, **22**, 86 (1959).

ON SOME SELF-RECIPROCAL FUNCTIONS

By

V. LAKSHMIKANTH

University College of Science, Osmania University, Hyderabad—Deccan-7

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Let the function $f(x)$ satisfy the integral equation

$$f(x) = \int_0^\infty J_p(xt) f(t) (xt)^{\frac{1}{2}} dt \quad (1)$$

where $J_p(x)$ is a Bessel Function of order $p \geq -\frac{1}{2}$. Then $f(x)$ is said to be a Self-Reciprocal function, for Hankel Transform, of order p and is denoted by R_p .

We know [1] that the function $f(x) = x^{-\frac{1}{2}}$ (2)

is R_p . Hence it is R_1 in particular.

It can be shown [2] that

$$\begin{aligned} & \int_0^\infty J_p(bt) \frac{J_{k_1}(a_1(t^2+z_1^2)^{\frac{1}{2}}) \dots J_{k_n}(a_n(t^2+z_n^2)^{\frac{1}{2}}) t^{p-1} dt}{(t^2+z_1^2)^{k_1/2} \dots (t^2+z_n^2)^{k_n/2}} \\ &= 2^{p-1} \Gamma(p) b^{-p} J_{k_1}(a_1 z_1) \dots J_{k_n}(a_n z_n) \cdot z_1^{-k_1} \dots z_n^{-k_n} \end{aligned} \quad (3)$$

if $\sum a_n < b$ and $a_i > 0$ for $i=1,2,3,\dots,n$.

Writing $b=x$ and $p=1$ we obtain from (3) that

$$\begin{aligned} & \int_0^\infty J_1(xt) \prod_{i=1}^n J_{k_i}(a_i(t^2+z_i^2)^{\frac{1}{2}}) \cdot (t^2+z_i^2)^{-k_i/2} dt \\ &= \prod_{i=1}^n J_{k_i}(a_i z_i) \cdot z_i^{-k_i} \cdot x^{-1} \end{aligned} \quad (4)$$

provided $\sum a_n < x$ and $a_i > 0$ for $i=1,2,3,\dots,n$.

The integral equation (4) can be written in the form

$$\begin{aligned} & \int_0^\infty J_1(zt) g(t, z_1, \dots, z_n) (xt)^{\frac{1}{2}} dt \\ &= \prod_{i=1}^n J_{k_i}(a_i z_i) z_i^{-k_i} x^{-\frac{1}{2}} = F(z_1, z_2, \dots, z_n) x^{-\frac{1}{2}}, \text{ say} \end{aligned} \quad (5)$$

$$\text{where } g(x, z_1, \dots, z_n) = \prod_{i=1}^n J_{k_i}(a_i(x^2+z_i^2)^{\frac{1}{2}}) \cdot (x^2+z_i^2)^{-k_i/2} \cdot x^{-\frac{1}{2}} \quad (6)$$

Taking $F_1(t) = t + t^{-1}$ and the function $g(t)$ given by (7) we have

$$h(x) = x^{-(\Sigma k_1 + \frac{1}{2})} \int_a^{1/a} \frac{n}{\pi} J_{k_1}(a_1 xt) (t^{\Sigma k_1} + t^{-(\Sigma k_1 + 2)}) dt \text{ is } R_1.$$

If we take $F_1(x) = x^2 / (1 + x^2)^{q+3/2}$ we find that $x^{-\frac{1}{2}} F_1(x)$ is reciprocal (1) to

$$x^{+\frac{1}{2}(q+2)} \frac{2^{-(q+1)/2}}{\Gamma^{-1} \frac{(q+3)}{2}} K_{\frac{1}{2}-q/2}(x)$$

and $x^{-\frac{1}{2}} F_1(1/x)$ is reciprocal (q) to the same function. *c. f.* [5] we thus see that

$$\begin{aligned} (h)(x) &= \int_0^\infty t^{3/2} (1+t^2)^{-\frac{1}{2}(q+3)} \cdot g(xt) dt \\ &= x^{-(\Sigma k_1 + \frac{1}{2})} \int_0^\infty \frac{n}{\pi} J_{k_1}(a_1 xt) t^{1-\Sigma k_1} (1+t^2)^{-\frac{1}{2}(q+3)} dt \text{ is } R_p. \end{aligned}$$

Other examples of this kind can easily be constructed.

REFERENCES

1. Mehrotra, B. M., (1935). A Brief History of Self-Reciprocal Functions. *Jr. Ind. Math. Soc.*, New Series, Vol. I, pp 209-227.
2. Bailey, W. N., (1936). Infinite Integrals involving Bessel Functions. *Proc. Lond. Math. Soc.*, Vol. 40 pp.
3. idem., (1931). On the solutions of some integral equations. *Jr. Lond. Math. Soc.*, Vol. 6, pp 242-247.
4. Narasimha Rao, V. V. L. (1957). On Self-Reciprocal Functions. *Proc. Nat. Acad. Sc. (Ind.)* Vol. 26, pp. 134-372.
5. Watson, G. N., (1922). Theory of Bessel Functions, pp. 434.

KINETICS AND MECHANISM OF REDUCTION OF CHLOROPLATINATE ION BY IODIDE ION IN NEUTRAL OR NEARLY NEUTRAL SOLUTIONS

By

BAL KRISHNA and K. C. TEWARI

Chemical Laboratories, University of Allahabad, Allahabad

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ABSTRACT

In this paper the mechanism of reduction of chloroplatinate ion by iodide ion in neutral or nearly neutral solutions has been studied and it has been found that the reaction is of second order with respect to chloroplatinate ion when the ionic strength of the solution is high, and of first order with respect to iodide ion. It has been suggested that a binuclear complex of platinum is formed which then reacts with iodide ion.

The mechanism of the reaction between chloroplatinate ion and iodide ion apparently conforms to the equivalence charge hypothesis of Shaffer^{1,2}. The reaction possesses finite speed and is amenable to kinetic measurement at the temperature of melting ice as well as ordinary temperatures in an acetate buffer. In higher acidic media the reaction is too fast to be measured kinetically. Though the mechanism apparently conforms to the equivalence charge hypothesis yet the charges of one of the reacting ions have to be modified in one of the rate determining steps to overcome the resistance of the reaction present in the form of coulombic repulsion.³

EXPERIMENTAL

One gramme of pure chloroplatinic acid was dissolved in 250 ml. of distilled water. The solution was standardised by estimating the amount of platinum as platinum sulphide⁴. A measured quantity of chloroplatinic acid solution containing the requisite amount of sodium acetate was taken in a conical flask blackened with Japan-black. The requisite quantity of potassium iodide was then quickly added to start the reaction. The liberated iodine was titrated at different intervals of time against the standard solution of sodium thiosulphate, with the help of a microburette. The temperature was controlled in a thermostat maintained at constant temperature. To increase the ionic strength of the reaction mixture, a neutral electrolyte was added. KCl, BaCl₂, K₂SO₄ and MgSO₄ were employed as neutral electrolytes.

The concentration of potassium iodide was generally kept large as compared to the concentration of chloroplatinic acid, and in any given experiment the order of the reaction has been calculated with respect to platonic salt alone. The order with respect to iodide was obtained by varying its concentration by a given factor and noting the variation in the constant calculated therefrom.

In general, it has been found that the order of the reaction with respect to chloroplatinate ion is two when the ionic strength of the solution is sufficiently high, as illustrated in Table I, while in those cases where the ionic strength is low, the second order constants show a rapidly decreasing value, as shown in Table II.

TABLE I

$[\text{H}_2\text{PtCl}_6]$	$= 1.59 \times 10^{-3} \text{ N}$	Temperature $= 25^\circ\text{C}$ pH $= 6.80$ $\mu = 0.8891$
$[\text{KI}]$	$= 2 \times 10^{-3} \text{ N}$	
$[\text{CH}_3\text{COONa}]$	$= 11.91 \times 10^{-2} \text{ M}$	
$[\text{K}_2\text{SO}_4]$	$= 0.25 \text{ M}$	

Time in minutes	ml. of N/400 sodium thiosulphate required by 5 ml. of the reaction mixture	$k_a' \times 10^3$ $(k_a' = a \frac{x}{(a-x)t})$
0	0.00	...
5	1.10	3.326
10	1.62	3.266
15	1.96	3.368
20	2.16	3.331
25	2.30	3.288
30	2.40	3.225
40	2.56	3.245
50	2.66	3.218
60	2.72	3.097
∞	3.18	

Average value $= 3.263$
 $k_a = k_a' \times f = 65.26 \text{ litre gm. equ.}^{-1} \text{ min.}^{-1}$

TABLE II

$[\text{H}_2\text{PtCl}_6]$	$= 1.59 \times 10^{-3} \text{ N}$	Temperature $= 25^\circ\text{C}$ pH $= 6.80$ $\mu = 0.1391$
$[\text{KI}]$	$= 2 \times 10^{-3} \text{ N}$	
$[\text{CH}_3\text{COONa}]$	$= 11.91 \times 10^{-2} \text{ M}$	

Time in minutes	ml. of N/400 sodium thiosulphate require by 5 ml. of reaction mixture	$k_a' \times 10^2$
0	0.00	
2	0.50	2.934
5	1.02	2.970
10	1.52	2.879
15	1.78	2.666
20	1.90	2.334
25	2.04	2.251
30	2.12	2.096
40	2.25	1.902
50	2.36	1.810
∞	3.18	

Average value $k_a' = 2.364$
 $k_a = 47.27 \text{ litre gm. equ.}^{-1} \text{ min.}^{-1}$

The order of the reaction with respect to iodide ion is found to be unity since the value of k_a is directly proportional to the concentration of iodide ion. This was studied at the temperature of melting ice at three different concentrations of potassium iodide as illustrated in Table III.

TABLE III

$[\text{H}_2\text{PtCl}_6]$	=	$3.1 \times 10^{-3} \text{ N}$	Temperature	=	0°
$[\text{CH}_3\text{COONa}]$	=	0.3 M	pH	=	7.0

$[\text{KI}]$	k_a	$k_3 = \frac{k_a}{[\text{KI}]}$
$2 \times 10^{-2} \text{ N}$	4.59 litre gm. equi. ⁻¹ min. ⁻¹	229.96 litre ² gm. equi. ⁻² min. ⁻¹
$4 \times 10^{-2} \text{ N}$	9.16 „ „	229.00 „ „
$8 \times 10^{-2} \text{ N}$	19.00 „ „	237.50 „ „

A perusal of the above table shows that the value of k_a is directly proportional to the concentration of iodide ion. Hence the total order of the reaction is three. The values of k_3 (i. e. the third order constant) are also given in Table III and it is seen that they are approximately constant.

Effect of Variation of Ionic Strength

An increase of ionic strength makes the value of k_a more steady. Though the value of k_a increases yet the increase in the constant is not so prominent as to clearly show an exponential dependence with ionic strength.

DISCUSSION

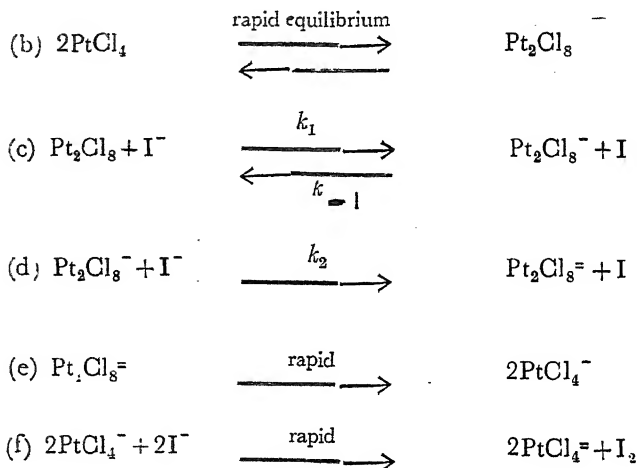
We have already seen that total order of the reaction is three, but this does not imply that mechanism of reaction is via ternary collision since the probability of ternary collisions is nil⁵. The reaction necessarily proceeds in steps so that ternary collisions are avoided. The most probable mechanism of the reaction is discussed below.

The total order of the reaction is three. The order is two with respect to platinum salt and one with respect to iodide ion. Since the order with respect to platinum salt is two, one has to assume the formation of a binuclear complex of platinum which is involved in the rate determining step. Binuclear complexes of platinum are of frequent occurrence⁶. This binuclear complex is the active species of the platinum salt which reacts with iodide ion giving rise ultimately to iodine and platinumous salt. The various stages of the reaction mechanism may be formulated below.

Normally platonic chloride exists in the form of chloroplatinic acid which being a strong acid will be present in the dissociated form. In presence of sodium acetate this reacts according to the following scheme



so that most of chloroplatinic acid will be converted into $PtCl_4$. Two molecules of this now react and form a binuclear complex of platonic chloride according to the scheme—



In the above formulation the velocity of the reaction will be dependent upon the steps (c) and (d), and it is obvious from the above scheme that the reaction will be of second order with respect to platinum salt. If we assume that the value of k_{-1} is very small in comparison to k_1 the back step in reaction (c) is negligible. In presence of large ionic strength k_2 will be quite large and the step (d) can also be taken to be a rapid one. In such a case the velocity will be dependent only upon k_1 and the velocity expression will be given by

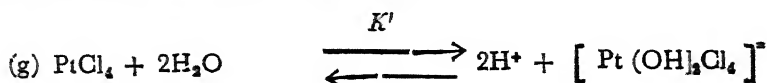
$$\begin{aligned}
 \frac{dx}{dt} &= k_1 [Pt_2Cl_8] [I^-] \\
 &= k_1 K_e [PtCl_4]^2 [I^-] \\
 &= k_3 [PtCl_4]^2 [I^-] \dots\dots\dots(1)
 \end{aligned}$$

where K_e is the equilibrium constant in step (b) and $k_3 = k_1 K_e$. Since in any given experiment $[I^-]$ is kept constant the above equation (1) can be written as

$$\frac{dx}{dt} = k_s [PtCl_4]^2 \dots\dots\dots(2)$$

However, when the ionic strength of the solution is low, step (d) will not be very rapid and Pt_2Cl_6^- may accumulate so that the back reaction in step (c) becomes material. In such a case, owing to the presence of back reaction the second order constant will decrease with time. This explains the decrease in the values of second order constants with time when the ionic strength is low.

We have now to explain the catalytic action of hydrogen ions as it is found that the velocity enormously increases at even the slightest increase in the concentration of hydrogen ions. The reaction is so fast that at a pH lower than 6.3, it is difficult to measure the kinetics of the reaction by ordinary methods. The reason for this is that at neutral or nearly neutral pH a part of platinic chloride is hydrolysed according to the following scheme.



The existence of such an equilibrium has been thoroughly established. For example it is well known that on dissolving anhydrous PtCl_4 in water compounds of $\text{H}_2 [\text{Pt}(\text{OH})_2\text{Cl}_4]$ type are formed.⁷ From reaction (g) it is clear that the concentration of PtCl_4 will be dependent upon the concentration of hydrogen ions. From reaction (g) we have.

$$[\text{PtCl}_4] = K' [\text{H}^+]^2 [(\text{PtCl}_4(\text{OH})_2)^-] \dots\dots\dots(3)$$

Substituting for $[\text{PtCl}_4]$ in Eq. (2) we obtain

$$\frac{dx}{dt} = k_a K' [\text{H}^+]^4 [(\text{PtCl}_4(\text{OH})_2)^-]^2 \dots\dots\dots(4)$$

That is the velocity will be proportional to the fourth power of hydrogen ions. This explains why there is a sudden rise in the velocity on increasing the acidity of the solution.

We may say a few words regarding the univalent oxidation principle of Weiss and Haber. According to this principle a simultaneous transfer of two electrons from an ion or a molecule is not possible and will take place in two steps. Now suppose the two consecutive steps of the transfer of electron are very fast and beyond kinetic measurement. In such a case the rapid and consecutive steps will in practice be equal to a single step.

REFERENCES

1. Shaffer, P. A., *J. Am. Chem. Soc.*, **55**, 2169 (1933)
2. Shaffer, P. A., *J. Phys. Chem.*, **40**, 1021 (1936)
3. Krishna, B., *J. Chem. Phys.*, **17**, 846 (1949)
4. Taimni, I. K. and Salaria, G. B. S., *Anal. Chim. Acta*, **11**, 329 (1954)
5. Moelwyn Hughes A. E., *Physical Chemistry*, p. 53 (1957)
6. Emeleus H. J. and Anderson, R. C., *Modern Aspects of Inorganic Chemistry* p. 131.
7. Sidgwick, N. V., *Chemical Elements and their Compounds*, Vol. II, p. 1615.

A STUDY OF THE FORMATION OF PIGMENTS BY *SERRATIA MARCESCENS*

By

KRISHNA BAHADUR and J. N. DUBE

Chemistry Department, University of Allahabad and Animal Nutrition Division, Indian
Veterinary Research Institute, Izatnagar, U. P.

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ABSTRACT

"The pink colour of *Serratia marcescens* fades on incubation at 35°C and on ageing. Low pH, iodide, bromide, borate and sulphite ions inhibit the formation of pigment in the organism but presence of calcium carbonate or beef extract help in the synthesis of the pigment. Of the metallic ions copper, nickel, iron and cobalt favour the formation of the pigments. Presence of molybdate ions in the culture medium profoundly influences the pigment formation in *S. marcescens* and a greenish blue pigment is formed in the organism instead of the usual pink pigment.

The red colour developed by *Serratia marcescens* during fermentation has been studied from many aspects. Wrede and Rothhaas (1) have worked out the pigment to be a tripyrrylmethene. Aerobic culture of the bacterium below 34°C or in anaerobic culture no pigment is formed. Still (2) found that addition of unsaturated fatty acids to the basal medium accelerated pigmentation at 27°C and permitted up to 42°C in aerobic culture and induced pigment formation in anaerobic culture between 27°C—38°C. Kwapinski and Pietraskiewicz (3) found that phenanthrene alkaloids brought about complete inhibition of pigmentation. Novelli (4) could restore the pigment producing power of the microorganism on agar without chlorophyll and even to a greater degree in the presence of chlorophyll by the ultraviolet light of 2537 Å. 1% Casein hydrolyzate and glutamic acid (5) inhibited the pigmentation when the microorganism was grown on Bunting's medium without phosphate. Weiss (6) observed that the red colour of *Serratia marcescens* is due to a compound closely related to tripyrrylmethenes. In the present paper we have studied pigment formation under different conditions—different pH and ions, concentration of phosphate, and different carbohydrates. The most notable study was in case of molybdenum in which colour deviated from pink to orange or greenish blue according to the age of the culture.

EXPERIMENTAL METHODS

The basal medium in which *Serratia marcescens* was grown is of the following composition KH_2PO_4 0.15g; K_2HPO_4 0.35g; $(\text{NH}_4)_2\text{SO}_4$ 0.17g; MgSO_4 0.08g; H_2O 100 ml. It contained phosphate 0.292 gm per 100 ml. The pH value of all the culture media employed in the experiments was adjusted to 7 unless otherwise

stated. Concentration of sucrose was 3 g. per 100 ml, whereas the concentration of other carbohydrates is stated (vide table.) In some experiments calcium carbonate was also added. Acidic and basic ions were added in quantities of 50 mg ions and 1 mg ion respectively. Only A. R. Chemicals were used in the experiments and their purity was examined before use.

The bacterium was obtained from U. S. Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Illinois. It grew in deep-pink colonies. The cultures were inoculated with the help of platinum loop.

Observations were also made supplementing the acid hydrolyzates of agricultural waste materials like bagasse, wheat straw, wheat bran, rice straw and rice polishings with beef-extract.

Molybdenum experiments :—The basal medium was fortified with 50 mg ion of molybdenum (as MoO_3) in the form of sodium molybdate and was distributed in 200 ml aliquots in several 500 ml pyrex flasks. The cultures were sterilized and inoculated. The pigment formation started after two days. At first pink colour appeared and later it changed to greenish blue colour after 45 days. 200 ml of the culture was taken at this stage, centrifuged and the residue washed once with distilled water to remove the bulk of the growth medium. The residue was transferred in a silica crucible and dried to constant weight in vacuum dessicator. The dry weight of the sample thus obtained was used as a basis for pigmentation content.

EXTRACTION OF PIGMENTS

From other five flasks 1000 ml of the culture were taken and centrifuged in several lots. The residue comprising of bacterial cells was dried in vacuum, removed by means of a glass rod with a freshly broken end and transferred to a small mortar containing approximately one gram of hydrochloric acid treated fine silica sand. It was ground with a pestle until a homogeneous mixture resulted that showed no streaking on further grinding. It took 40 minutes. The mixture was moistened with a few c. c. of 80% aqueous acetone and rubbed up, whereupon it could be transferred to the filter completely and extracted with fresh solvent. After several washings the residue was pure white and showed no trace of pigments.

The filtrate was transferred to a separating funnel and washed with a 20 ml. portion of chloroform followed by three 10 ml. portions. Practically all color went into the chloroform layer. Chloroform layer was separated and evaporated to get the mixture of pigments.

RESULTS

Visual observation of color is tabulated in the table. Red color is subclassified into five categories just pink, light pink, pink, deep pink and very deep pink or red. Molybdenum containing cultures showed a marked variation from usual red colour. It became yellow or orange after 32 days and gradually changed into greenish blue in the final stage. This was observed in a set of six flasks each containing 200 ml. of the culture. This was separated and 4.0 mg of light green pigment were obtained from 1000 ml. of the culture, 200 ml of the culture yielded 35 mg. of dry weight of bacterial cells. On the basis of dry weight of bacterial cells 2.3% of the pigments are produced. It was found that cultures in general were showing depression in the intensity of color when these were placed in incubator at 35°C. The pigmentation was much more intense when kept at room temperature which ranged between 25° to 28°C. With the ageing of culture the rate of pigmentation fell. In some cases the aged culture became almost colorless.

Colour produced in the culture after fermentation by *Serratia marcescens*

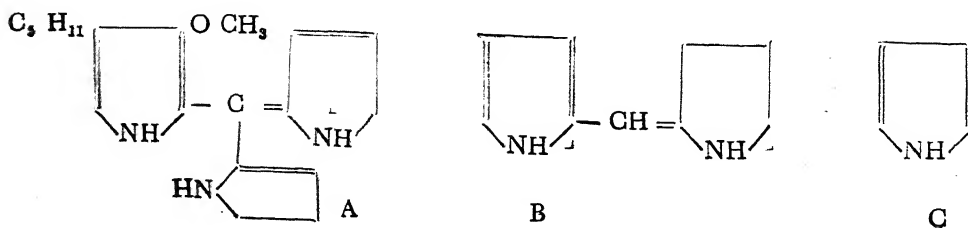
Colour	Specific substrate or ion
Colourless	... pH 6.0 and 7.5; Mannitol 3.19% Sorbitol 3.19%, I (50 mg/100 ml), Br (50 mg/100ml); B_4O_7 (50 mg/100 ml); SO_3 (50mg/100 nil).
Light pink	... Phosphate (0.584%); Sucrose (6.0%), Xylose (3.12%), Fe^{+++} (1mg/100ml); Co^{+++} (1mg/100ml).
Just pink	... Phosphate (0.584%); pH 5.5; Fructose (3.16%), Cu^{++} (1mg/100ml), Ni^{+++} (1mg/100ml) and (0.438%).
Pink or wine red	... pH 5.0 and 6.5; Sucrose (1.5%, 4.5%; Lactose (3.0%); (50mg/100ml); Mo (50mg/100ml), 30%);
Deep pink	... Phosphate (0.292%); $CaCO_3$ (1.0%); Glucose (3.155%); Glycerol 3.225%; S_2O_3 —(50mg/100ml) $CaCO_3$ (1.5%)
Very deep pink or red	... $CaCO_3$ (2.0%); 2.5%; 3.0%.
Yellow or Orange	... Mo(50mg/100ml) 32 days.
Greenish blue	... Mo(50mg/100ml) 35 days.
Blue	... Mo(50mg/100ml) 45 days.

The acid reaction of the culture does favour colour formation but addition of calcium carbonate enhances pigment production. In the latter case a pink scum was also noticed over the surface of the culture medium. Iodide, bromide, borate and sulphide inhibit the pigment formation. Copper, nickel, iron, cobalt and molybdenum react favourably. However, molybdenum changes the color of the pigment from red to greenish blue, the change occurred between 25th day and 35th day.

The pigmentation became more prominent when aminoacids from beef extract were incorporated in the media containing acid hydrolyzates of agricultural wastes. Previous to this supplement these cultures were either colorless or light pink.

DISCUSSION

According to Wrede the red pigment of *S. Marcescens* is due to the tripyrrymethenes (A)



This may undergo cleavage into a dipyrromethene (B) and a pyrrole (C). This mechanism studied by Corwin and Andrews (6) is of biological importance. Dipyrromethenes are usually faint yellow whereas dipyrromethenes are colorless. Again two dipyrromethenes may unite to give a molecule of tetrapyrromethenes. Biliverdin and glaucobilin belonging to the latter group are known to have absorption bands 650 m μ and 635 m μ and have green and blue colour respectively. Molybdenum in some way possibly brings about the cleavage of the molecule of tripyrromethenes giving rise to greenish-blue pigment. Separation of the pigments as mentioned in the paper warrants further research into the chemical nature of the pigments through chromatographic analysis and microanalysis. It is expected that this will throw light into the problem.

SUMMARY

1. Cultures showed fading in the colour when grown in incubator at 35°C, Ageing also recorded a similar fall in pigmentation.
2. Low pH, iodide, bromide, borate and sulphite inhibited the formation of pigment but calcium carbonate and beef extract, enhanced the pigment production.
3. Cu, Ni, Fe & Co favour the pigment formation. Molybdenum in the form of sodium molybdate further changed the colour of the pigment from red to greenish blue. 2.3% of greenish blue pigments on the basis of dry weight of bacterial cells were isolated.

REFERENCES

1. Wrede, F. and Rothhaas., *Z. physiol Chem.* 219, 167 (1933)
2. Still J. L., *Australian J. Sci.*, 16, 278 (1953).
3. Jerzy Kwapinski and Helena Pietrakiewicz *Med. Doswiad Czalna i Mikrobiol*, 5, 159-64 (1953)
4. Amato Novelli, *J. Bact.* 65, 479-80 (1953).
5. Eugene D. Weinberg, *J. Bact.* 62, 785-92 (1951).
6. Charles M. Weiss, *J. Cellular Comp. Physiol* 34, 467-92 (1941).
7. Corwin, A. H., and Andrews, J. S., *J. Am. Chem. Soc.* 58 1036 (1936).

STUDIES IN CHROMIUM ARSENATE SOL

PART I : SURFACE TENSION, VISCOSITY, CONDUCTIVITY AND STABILITY OF THE CHROMIUM ARSENATE SOL WITH THE PROGRESS OF DIALYSIS

By

P. C. JAIN and S. N. BANERJI

Chemical Laboratories, University of Saugar, Saugar

[Received on 14th July, 1959]

ABSTRACT

In a previous communication¹ we have studied the surface tension, viscosity, conductivity and stability of chromium tungstate sol. We have shown therein that there is an increase in the surface tension of the sol with dialysis and the viscosity as well as the values of ϕ (fraction of the total volume of sol particles to that of the whole system) first decrease, then increase exponentially and finally abruptly, the later being due to increased rate of formation of loose aggregates leading finally to gel formation. Conductivity measurements show that initially there is a higher conductivity value produced by gegenions while later on when the sol attains sufficient purity the conductivity decreases slowly until it approximates to a constant value. The stability of the sol decreases rapidly with purity and finally gel is formed.

Our observations with chromium arsenate sol are being discussed here.

Holmes² prepared chromium arsenate sol, while Prakash and Dhar³ studied the conditions of jelly formation of this sol. We have made here a detailed study of the surface tension, viscosity, conductivity and stability of this sol with the progress of dialysis.

EXPERIMENTAL

The sol was prepared by adding a solution of 5% sodium arsenate from a burette to a M/4 solution of chromium chloride with continuous shaking until the slight precipitate formed got peptised with excess of chromium chloride. It was then filtered and kept for dialysis. The composition of the sol at different stages of purity has been determined by the usual standard methods and the results are reported as the percentages of Cr_2O_3 , arsenate and chloride respectively.

Measurements of surface tension, viscosity, conductivity and stability of the sol at 30°C were made as described in the previous communication.¹

RESULTS

TABLE I

Composition of the sol with dialysis.

Stages of dialysis	days of dialysis	percentages of		
		Cr ₂ O ₃	Arsenate	Cl-
I	1	1.3050	0.4662	0.4721
II	3	0.8852	0.3713	0.1912
III	5	0.7540	0.3420	0.0502
IV	9	0.7265	0.3383	0.0212
V	12	0.7151	0.3355	0.0115
VI	16	0.7140	0.3311	0.0089
VII	18	formed gel		

The sol at different stages of dialysis is marked as I, II, III, IV, V, VI and VII.

TABLE II

Surface tension, viscosity, and conductivity of the sol.

Temperature 30°C

	Surface tension in dynes	Viscosity in centipoises	Specific cond. $\times 10^3$ mhos
Water	72.1	0.8007	---
Stages of dialysis	Sol	Sol	Sol
I	69.8	0.8541	13.7500
II	67.6	0.8220	6.4330
III	70.0	0.8313	1.9430
IV	70.9	0.8544	0.8069
V	71.9	0.9891	0.3666
VI	72.0	3.4271	0.2821

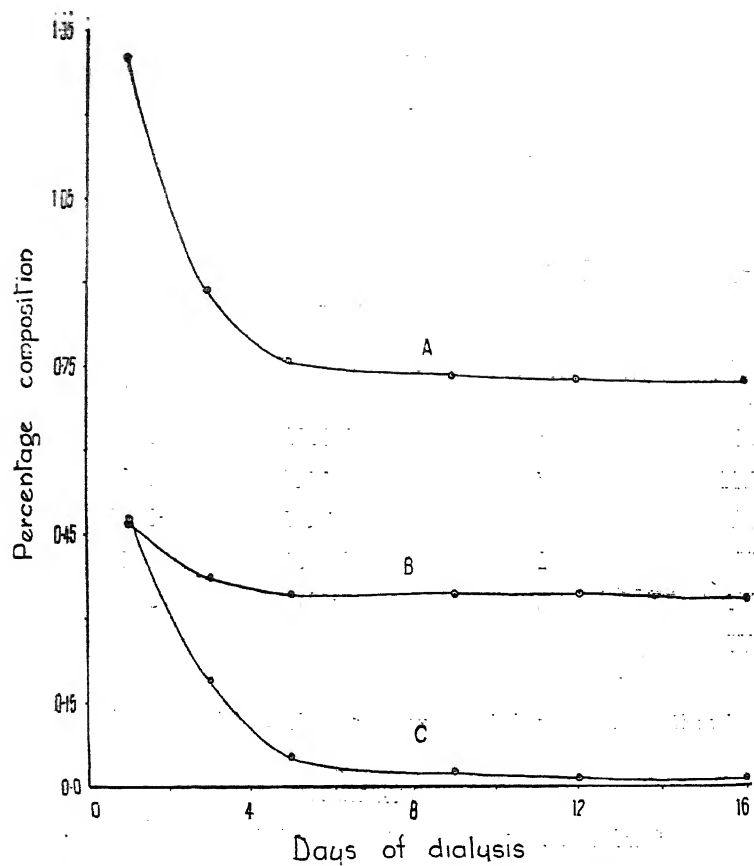


Fig. 1. Showing the percentage composition of the sol at different stages of dialysis Curve A : Cr₂O₃ ; Curve B : Arsenate ; Curve C : Chloride.

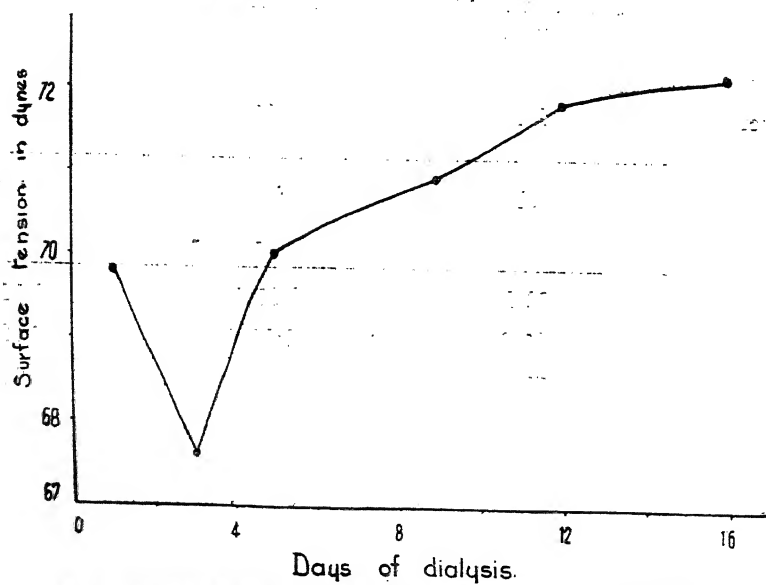


Fig. 2. Showing the surface tension of the sol at different stages of dialysis.

TABLE III
The values of ϕ^* using Einstein's ($n_r = 1 + 2.5\phi$) and
Guth-Simha's ($n_r = 1 + 2.5\phi + 14.1\phi^2$) equations :

Stages of dialysis	Einstein's equation	Guth-Simha's equation
I	0.02668	0.02351
II	0.01065	0.01001
III	0.01529	0.01350
IV	0.02670	0.02353
V	0.09376	0.06801
VI	1.3120	0.40190

*[This notation has unfortunately been omitted after the values of ϕ (i) in 4th line, second para and (ii) under table IV in the final printing of the previous paper¹.]

TABLE IV
Coagulation values with M/10 potassium sulphate solution.
Volume of sol taken = 5.0 ml. Total volume = 10 ml.

Stages of dialysis	K ₂ SO ₄ in ml.	Observations after mixing
I	2.0	No coagulation even after 2 hrs.
II	1.0	Coagulation after 2 mins.
III	0.57	Coagulation after 2 mins.
IV	0.33	Gelation starts slowly.
V	0.21	Gelation starts at once.
VI	0.10	Gel formed at once.

DISCUSSION

The surface tension in the initial stage is smaller (table II) due to the presence of charge on the sol particles. As these are removed in the form of impurity, the surface tension increases until it attains a static value.⁴

Of the three stages in the changes of viscosity (table II) and also in the values of ϕ (table III), the initial decrease is due to the removal of charge from the surface

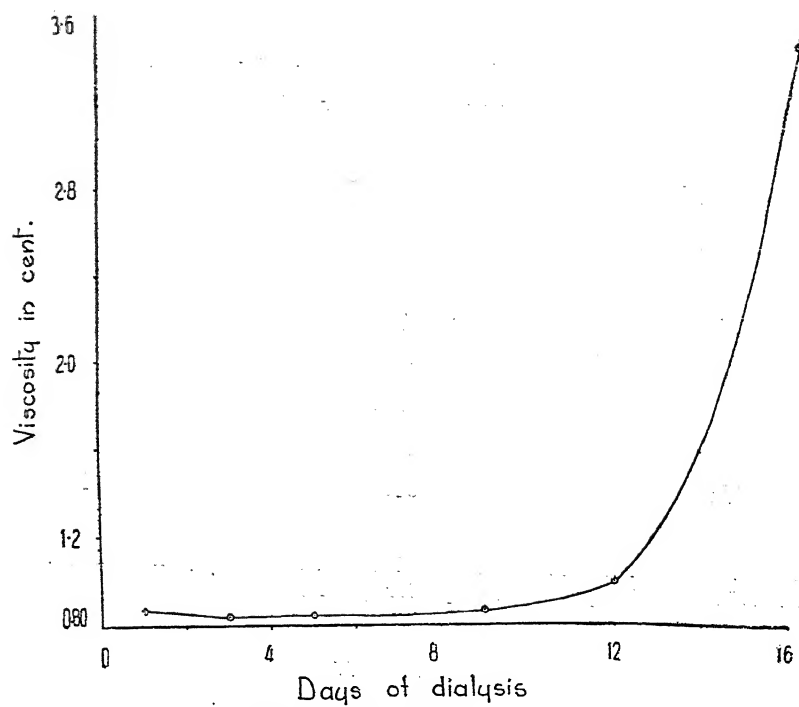


Fig. 3. Viscosity of the sol with the progress of dialysis.

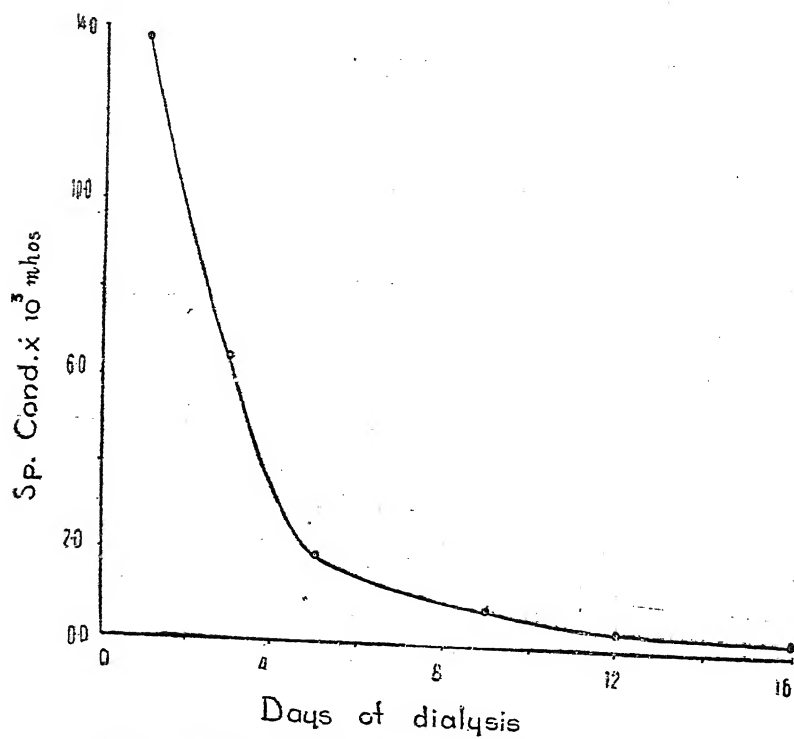


Fig. 4. Specific conductivity of the sol at different stages of dialysis.

of the sol particle and the exponential increase is mainly due to the tendency of aggregation. The abrupt increase is because of the increased rate of aggregation leading to the formation of loose aggregates having high values of ϕ that increase the resistance to flow.

The specific conductivity of the sol initially is very high. It is because of the presence of chromium, chloride, hydrogen and sodium ions as impurities. As the dialysis progresses these stabilising ions having high ionic velocities are gradually removed and hence the conductivity decreases. When the sol attains sufficient purity, the decrease in conductivity is less. This is due to the decrease in the mobility of the micelles because of increased radius resulting in slowing down their velocities.

As the charges on the sol particles are removed with dialysis, the stability also decreases (table IV) and the sol becomes more and more unstable and finally gel is formed.

REFERENCES

1. Jain P. C. and Banerji S. N., *Proc. Nat. Acad. Sci., India*, **27**, 147 (1958).
2. Holmes, *J. Amer. Chem. Soc.*, **38**, 1980 (1916).
3. Prakash S. and Dhar N. R., *J. Ind. Chem. Soc.*, **6**, 396 (1929).
4. McBain, J. W., *Colloid Science, New York* 54-8, 114 (1950).

CHEMICAL EXAMINATION OF THE SEEDS OF JATROPHA CURCAS LINN.—PART II

STUDIES ON MUCILAGE

By

A. SINHA

Chemical Laboratory, Medical College, Agra

[Received on 28th September 1959]

The seeds of *Jatropha Curcas* Linn. (N. O. *Euphorbiaceae*) (Eng. Angular Physic Nut) commonly known as Jangali erandi in Hindi and Kanana erandi in Sanskrit is an evergreen plant common in waste places throughout India. The seeds are acro-narcotic and have been used in Ayurvedic system of medicine for its strong purgative and antiseptic actions^{1,2}. The chemical examination of the seeds revealed the presence of an oil, mucilage and colouring matters. The seeds yield 32.7% a pale yellow oil containing jatrophic acid as the active principle. The physical and chemical constants of the seed and the seed oil have been investigated in detail and reported earlier by the author.³ The seeds of *Jatropha Curcas* Linn. contained 2.7% of reducing sugars and the presence of glucose, arabinose, xylose, galactose and rhamnose has been established by paper chromatography. The component fatty acids of the oil were examined and the presence of myristic 1.80; palmitic 13.6; stearic 18.2; linoleic 29.32; aridic 0.6 and oleic 36.48% respectively was established by bromination and ester fractionation methods of Hilditch.⁴ The composition of the oil is in accordance with that shown by the generalisation of Hilditch⁴ for most other members of *Euphorbiaceae* family and also as reported by Kartha and Menon.⁵ The unsaponifiable matter of the oil consisted of the common phytosterol and sitosterol and was identified by its melting point, acetyl derivative and by colour reactions. Studies on the mucilage have been described in the present communication.

The freshly extracted mucilage was dirty white in colour and fibrous in nature. On complete incineration it gave 4.16% greyish white ash containing 1.88% iron and 1.48% magnesium. The mucilage on hydrolysis with 3% oxalic acid showed the presence of arabinose, xylose and aldobionic acid. The total percentage of reducing sugars was 18.4%. The residual mucilage was then next hydrolysed with 2N. sulphuric acid when the presence of xylose, galactose, rhamnose and galactouronic acid was detected. The total percentage of reducing sugars in the hydrolysate at this stage was 22.3%. The mucilage left after the above two hydrolyses was further hydrolysed with conc. sulphuric acid when only 19.5% of glucose was obtained. The presence of cellulose in the mucilage was thus also indicated.

EXPERIMENTAL

Extraction of Mucilage

0.5 Kg. of the dried and powdered seeds were exhaustively extracted with petroleum ether (b. p. 40°–60°) and acetone (2 : 1 v/v) to remove oil, colouring matters and other organic impurities. The defatted seeds were then allowed to soak in a mixture of 980 c. c. distilled water and 20 c. c. glacial acetic acid at 30° for 16 hours. The addition of 2% of glacial acetic acid increased the yield of mucilage and prevented its hydrolysis during further extraction. The contents were then mechanically stirred for 20 hours and filtered through cotton wool. The filtrate

was mixed with an excess of absolute alcohol when a stringy mass was obtained. It was separated, washed, dried and weighed, (yield 12.2%).

Purification of the mucilage

The crude mucilage was first dissolved by boiling in acidified (with 6% acetic acid) distilled water and filtered. The filtrate was mixed with absolute alcohol and the mixture stirred as before when the mucilage was precipitated out. It was separated, dried and then again successively refluxed with petroleum ether, ether, benzene, chloroform and finally with absolute alcohol to remove all other organic impurities. Finally it was dried in vacuum and on ultimate analysis was found to contain C, 39.2%; H, 8.16% (the rest would be oxygen and ash). The equivalent weight of the pure mucilage was found to be 1200 approx. by the titration method. The mucilage on complete incineration at 500° for 2 hours in a muffle furnace left a greyish white ash (yield 4.16%) containing 1.88% iron and 1.48% magnesium. The viscosity of the gelatinous solution of the mucilage was determined at different pH and the maximum values were noted at pH 6.0. On ageing the solution, the viscosity decreased rapidly. The mucilage was insoluble in water and organic solvents.

Hydrolysis of the mucilage with 3% oxalic acid

The mucilage (20 g.) was completely hydrolysed by heating with 3% oxalic acid solution (100 c. c.) on a water bath for 20 hours when the hydrolysis was complete as determined by following the course of hydrolysis by taking out test portions of the reaction product from time to time. The solution was filtered, residue washed and the washings were mixed with the filtrate. This solution was then neutralised with barium carbonate to convert sugar acids into soluble barium salts and to remove excess of oxalic acid as barium oxalate. The solution was filtered, barium oxalate discarded and the solution was concentrated to a syrup under reduced pressure. The syrup was shaken with methyl alcohol and filtered. The filtrate was tested for sugars while the residue for acids. The filtrate was evaporated to dryness, residue dissolved in water and solution made upto 100 c. c. The quantitative determination of the sugars in the solution indicated that 18.4% of reducing sugars was present in the solution and sugars were identified to be arabinose and xylose by paper chromatography by the method described under separation and estimation of sugar components of *Allium Cepa*, Linn.⁶ The presence of these sugars was further confirmed by preparation of their osazone derivatives when two osazones of m. p. s. 163° and 200° corresponding to the phenylosazones of xylose and galactose respectively were obtained.

The barium salt of the sugar acid was estimated quantitatively and the percentage of barium corresponded to the percentage of barium of the corresponding salt of aldobionic acid. (Calculated value for barium in barium salt of aldobionic acid is 16.18%). Found barium 16.08%. The barium salt was further oxidised by conc. nitric acid and the oxidation product was found to be mucic acid (m. p. 210°) thereby confirming aldobionic acid.

Hydrolysis of the mucilage with 2 N sulphuric acid

The insoluble part of the mucilage left after the separation of the water soluble products of oxalic acid hydrolysis was further hydrolysed by 2 N. sulphuric acid. The hydrolysis was complete in 36 hours as determined by test portions taken out at regular intervals during the hydrolysis. The products of hydrolysis

were separated into sugars and acid portions as in the case of hydrolysis with oxalic acid. The excess of sulphuric acid was removed as insoluble barium sulphate. The mucilage left at this stage was kept for hydrolysis with conc. sulphuric acid.

The quantitative determination of sugars indicated the presence of 22.3% of reducing sugars in the solution and the sugars were identified to be xylose, galactose and rhamnose by paper chromatography by the procedure mentioned under oxalic acid hydrolysis. The presence of these sugars was further confirmed by preparing their osazone derivatives when corresponding phenylosazones were obtained.

Barium content of the barium salt of the acid was quantitatively estimated as before when the percentage of barium corresponded to the percentage of barium salt of galactouronic acid. Found barium 26.0%.

Hydrolysis of mucilage with conc. sulphuric acid

The residue of mucilage left after the separation of the water soluble products on hydrolysis with 3% oxalic acid and 2 N. sulphuric acid was finally hydrolysed with conc. sulphuric acid. The separation of the products of hydrolysis after filtration and subsequent neutralisation of the filtrate with barium carbonate showed the presence of 19.5% glucose. The estimation of glucose was done by paper chromatography and confirmed by preparing its osazone derivative. The different percentages of reducing sugars obtained in the hydrolysates obtained above indicates that cellulose was thus also present in the mucilage.

ACKNOWLEDGMENT

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REFERENCES

1. Nadkarni, "Indian Materia Medica", Popular Book Depot, Bombay, (1954).
2. Chopra, "Indigenous Drugs of India", Art Press, Calcutta, (1933)
3. Sinha, A., *Jour. and Proc. Inst. Chem. (India)*, **31**, 213 (1959).
4. Hilditch, "The Chemical Constitution of Natural Fats" Chapman and Hall Ltd., London, (1956).
5. Kartha and Menon, *Proc. Indian Acad. Sciences*, **18A**, 160 (1944).
6. Sinha, A. and Sanyal, A. K., *Curr. Science*, **28**, No. 7, 281 (1959).

THE PREPARATION OF FERRIC SUCCINATE GELS FROM FERRIC SUCCINATE SOLS

By

S. K. BOSE and S. P. MUSHRAN

Chemical Laboratories, The University, Allahabad

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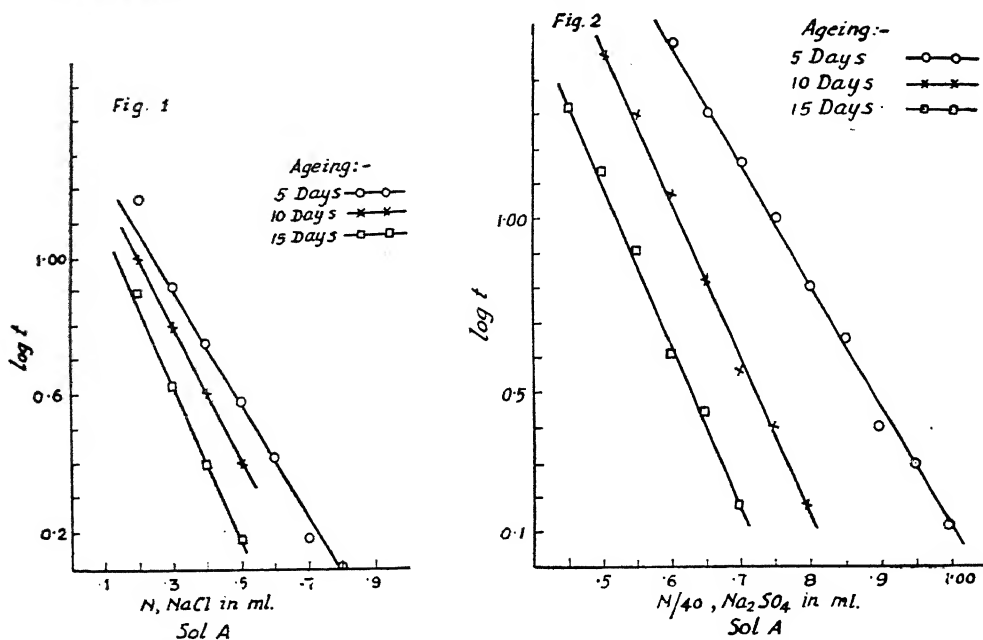
ABSTRACT

Ferric succinate sols have been prepared by dispersing freshly precipitated ferric succinate in succinic acid. The sols yield transparent gels with electrolytes of suitable concentrations. The process of gelation is governed by the relation $\log t = A - Bc$ where t is the gelling time and c is the concentration of the gelating electrolyte. It has been shown that the value of A in this equation is a measure of the stability of the sols whilst B describes the specific nature of the gelating ion. The ferric succinate sols, though capable of yielding gels, show various lyophobic characteristics.

In a publication from this laboratory the preparation of ferric succinate gels obtained by the interaction of sodium succinate and ferric chloride solutions of suitable concentrations has been described (1). In a recent publication (2) it has been shown that the precipitate separating out as a result of the interaction of the sodium salt and the metal salt solution develops into a gel, when the added sodium succinate approaches the equivalent amount. In other publications the conditions of the preparation of thorium (3), zirconium (4), and titanium (5) succinate gels have been investigated. In all such cases where the gels are formed by metathetical process the sol is in a transient state which may be so short as to be experimentally undetectable.

A sol of ferric succinate could be prepared by dialysing a mixture of sodium succinate and the metal chloride, when the latter is in excess. The sol thus produced is in no way a concentrated one and it is difficult to make it free from

chloride ions. It is thus very unstable and precipitation takes place during purification by dialysis. A different method had therefore to be adopted for its preparation.



Iron succinate was first precipitated by the interaction of ferric chloride and excess of sodium succinate. The freshly precipitated iron succinate was thoroughly washed in a Buchner funnel till the wash water was free from succinate and chloride ions. The washing was completed within a day to avoid ageing of the precipitate. The fresh precipitate was shaken with requisite quantities of succinic acid in a Microid Flask Shaker and the peptisation was complete within a few hours. Transparent wine red sols were thereby obtained. The sols could be easily coagulated with electrolytes and under suitable conditions gave transparent and stable gels. The transparency of the sols during gelation was so well maintained that no variation of the absorption of light was noticed when measured by a Klett Photoelectric Colorimeter.

In this paper we are recording our observations on the effect of purity and ageing of such sols on their gelation.

EXPERIMENTAL

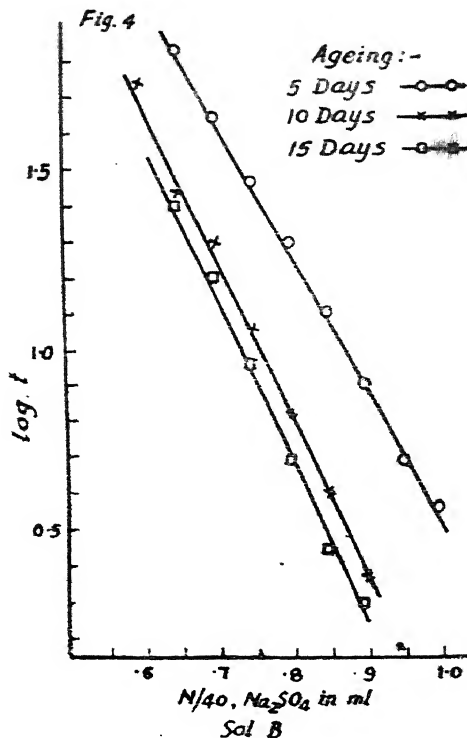
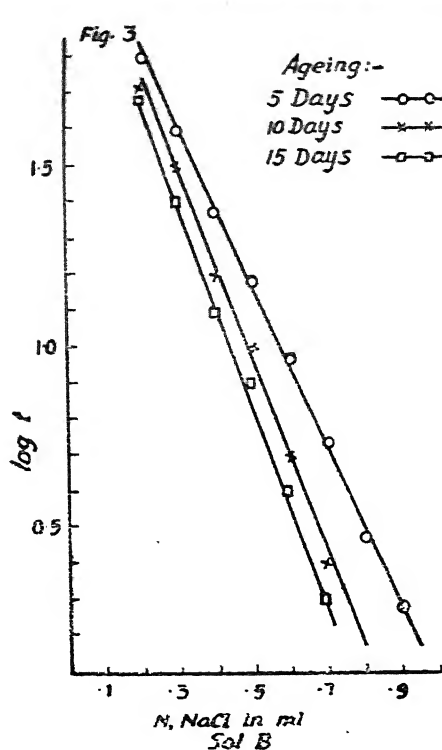
Three samples of the sols were prepared as described above, with different amounts of succinic acid. The iron content in each sample was kept the same by estimating iron from the peptised sols by the usual methods, and then diluting it as desired. Sols A, B, C, thus formed were of different purities according to the amount of succinic acid added for peptisation. The sol containing the least amount of succinic acid was the purest. Each sample had the following composition:

Total volume = 800 ml.

Total Fe^{3+} content = 0.0342 gm. atom

Sol	M/2 Succinic acid.
A	200.0 ml.
B	300.0 ml.
C	400.0 ml.

The sols were allowed to age at room temperature varying roughly from $28^{\circ} - 32^{\circ} \text{C}$. The gelation was observed at a constant temperature of $32 \pm 0.1^{\circ} \text{C}$ at three different stages of ageing.

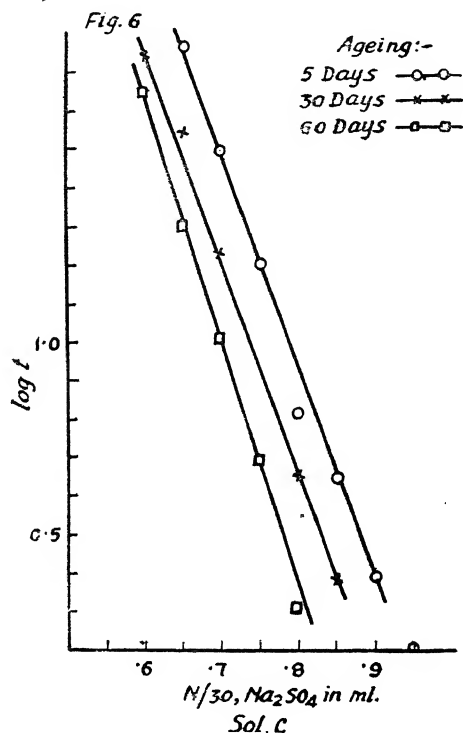
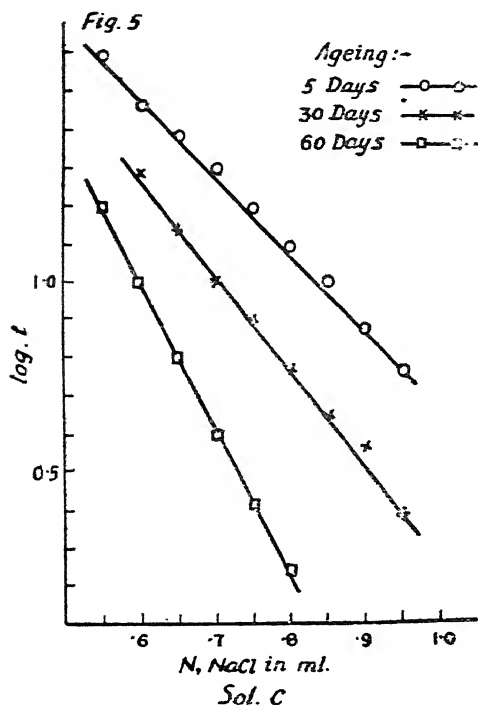


Two electrolytes, sodium chloride and sodium sulphate were used in varying amounts to effect gelation and the gelling times were recorded by the method described in one of our recent publications (6). The sols were preserved in Jena bottles and measurements were carried out by a micropipette wherever necessary. The results of the measurements were represented graphically in Figs. (1-6) where the logarithm of the gelling times have been plotted against the concentrations of the gelating electrolytes.

DISCUSSION

A perusal of the figures (1-6) show that the ferric succinate sols, being positively charged, the gelling time with sodium sulphate is less than that with sodium chloride, as with these sols the anions are effective in the gelation process. Further as the purity of the sol is decreased by increasing the amount of succinic acid employed for peptisation a greater amount of electrolyte is necessary for the purpose of gelation. This effect is more prominent with the uni-univalent electrolyte, sodium chloride, than that with sodium sulphate containing bivalent anion. These results of ours are similar to that observed in the coagulation of several lyophobic sols, where the variation in the precipitation values of the polyvalent coagulating ions do not change to the extent that is observed for monovalent coagulating ions. The results are therefore in conformity with the Whetham's rule for the coagulating ions of varying valencies.

It is interesting to note that the plot of $\log t$ and c is a straight line suggesting a relation $\log t = A - Bc$. This relation is very similar to the equation derived by Reerink (7) for slow coagulation except that he obtained $\log c$ instead of c . The agreement between the two relations supports the idea that gelation is a slow coagulation.



It will be seen that the value of A which is represented by the intercept of the curves on the Y axis has a tendency to increase with increasing amount of succinic acid present in the sol and is independent of the nature of the electrolyte used for the formation of the gel. The value of B represented by the slope of the straight line is greater for bivalent anion sulphate than for monovalent chloride. The results, therefore, lead us to the interesting conclusion that for these sols the value of A is the measure of the stability of the sols, that is, it expresses the value of the logarithm of the time which will be taken when the sol will set by themselves without the addition of the gelating electrolyte. The value of B however is described by the specific nature of the gelating ions. The results therefore, prove that the sols become more stable with the increasing amount of succinic acid and hence require a greater amount of electrolyte for gelation. Again, all the three samples of the sols tend to gellify more quickly when allowed to age. The effect is more prominent for the sols containing smaller amount of succinic acid used for peptisation. A perusal of the figures show that the value of A decreases with ageing whilst the value of B increases. It is therefore evident that the ferric succinate sols investigated in this paper are more susceptible to the action of electrolytes on ageing. This decrease of stability with age is a characteristic property shown by several lyophobic sols investigated by Ghosh and coworkers (8). The sols of ferric succinate investigated in this paper, though capable of yielding gels, have therefore certain properties common to those of lyophobic sols.

The authors are grateful to Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I. for encouragement and interest during the progress of this work.

REFERENCES

1. Prakash, S. and Mushran, S. P., *Nature*, **163**, 878 (1949).
2. Bose, S. K. and Mushran, S. P., *Koll-Zeit.*, **154**, 141 (1957)
3. Upadhyay, Y. D. and Mushran, S. P., *Naturwiss*, **45**, 514 (1958)
4. Upadhyay, Y. D. and Mushran, S. P., *Proc. Nat. Acad. Sci., India*, **28A**, 124 (1959)
5. Upadhyay Y. D., *Unpublished work*.
6. Bose, S. K. and Mushran, S. P., *Proc. Nat. Acad. Sci., India*, **27A**, 21 (1958)
7. Reerink, H., 'Colloid Science', Kruyt, H. R., **1**, 365 (1952)
8. Ghosh, S., *Presidential Address : Section of Chemistry, 45th Indian Science Congress*, Madras, (1958)

POLAROGRAPHY OF THIOMALIC ACID (PART II)

(Investigations in Neutral and alkaline solutions)

By

S. K. TIWARI and R. C. KAPOOR

Chemical Laboratories, University of Allahabad, Allahabad

[Received on 12th October, 1959]

ABSTRACT

Polarography of thiomalic acid has been studied in neutral and alkaline pH values. The investigations have been made in borax buffer (pH 9); ammonia buffer (pH 9) and phosphate buffer (pH 7).

The acid gives reversible anodic wave in all the media and undergoes an one electron change at the electrode.

The anodic wave appears to be due to the formation of a mercury thiomalic acid compound.

A compound of thiomalic acid and mercuric mercury has been isolated which gives a reversible cathodic wave. The half-wave potential of the wave is identical to the thiomalic acid anodic wave.

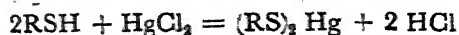
Polarography of thiomalic acid has been studied in alkaline and neutral media. These investigations are in continuation to those described by the authors¹ previously.

This paper deals with the details of polarographic study of thiomalic acid in borax buffer (pH 9) ammonia buffer (pH 9) and phosphate buffer (pH 7). The reaction taking place at the dropping mercury electrode during anodic depolarization has been studied and shown to be due to formation of a mercury sulphydryl compound. The compound has also been isolated and studied.

MATERIALS

Thiomalic acid was obtained as gift from Evans Chemetics Inc, New York (U. S. A.). The compound was 97% pure as determined amperometrically. Stock solutions of 0.1M and 0.01M thiomalic acid were prepared in double distilled water. Only freshly prepared solutions were used for investigations. All other chemicals used were of Analar or chemically pure grade. Mercury used in the dropping mercury electrode (D. M. E.) was first purified by chemical treatment and subsequently distilled twice.

The mercury compound of thiomalic acid was prepared by the interaction of equimolar solutions of 2 volumes of thiomalic acid with one volume of mercuric chloride (Analar) by weight. The mixture was shaken with ether. The ether extract was then evaporated to dryness giving colourless substance.



To determine the percentage of mercury present in the compound, the method described below was carried out for the estimation of mercury as sulphide².

Acidic solution of mercury compound was taken. A little ammonia was added to neutralise the acidity. Then 50 ml of 2N Na_2S solution (cooled to 5°C) and 100 ml of 2N HCl were added. The contents were boiled on a hot plate and subsequently cooled to room temperature. The precipitate of mercuric sulphide was filtered through G₄ sintered glass crucible, washed thoroughly with water and then with alcohol and ether successively. It was then dried at $100-110^\circ\text{C}$ and weighed after cooling in a desiccator.

The percentage of mercury experimentally found was 40.17% which agreed well with the theoretical value of 40.23%.

EXPERIMENTAL

Current-voltage curves have been taken at $30.0^\circ \pm 0.1^\circ\text{C}$. The dropping mercury electrode employing double distilled mercury was used as the indicator electrode and served as cathode. The anode was a saturated calomel electrode which also served as the reference electrode in all experiments.

The characteristics of dropping mercury electrode capillary used were: $m = 1.376 \text{ mg sec}^{-1}$, $t = 5.5 \text{ sec}$. (open circuit); $m^{2/3} t^{1/6} = 1.644 \text{ mg}^{2/3} \text{ sec}^{-1/2}$; $h = 40 \text{ cms}$.

The pH of the solutions was measured with Leeds and Northrup pH meter using a general purpose glass electrode.

RESULTS

Polarograms of thiomalic acid were obtained at pH 9 and 7 respectively. The anodic wave of the thiol compound is diffusion controlled as can be seen from observation in tables II and III. The plots of $\log \frac{id-i}{i}$ vs voltage give slopes of 0.0565 in borax buffer (pH 9); 0.057 in ammonia buffer (pH 9) and 0.057 in phosphate buffer (pH 7). The values agree fairly well with the theoretical value for one electron change at the electrode.

Thiomalic acid mercury compound has been prepared and analysed. Polarographic analysis gives a cathodic wave at borax, ammonia and phosphate buffers. The characteristics are identical to the thiomalic acid wave under identical conditions including the half wave potential.

Table I summarises the observations of different polarograms of thiomalic acid at different buffers.

TABLE I

Compound	Buffer	pH	Concentration $M \times 10^3$ (c)	Diffusion current (i_d) in μA	i_d/c	E_d in volts	Remarks
Thiomalic acid	$NH_4Cl + NH_4OH$	8.8	2.56	6.925	2.71	-0.520	at 30°C
" "	" "	8.8	5.00	13.525	2.71	-0.520	at 30°C
Mercury thiomalate $Hg(TS)_2$	" "	9.0	1.00	4.505	4.505	-0.522	"
Thiomalic acid	Borax + KCl	9.1	1.00	2.825	2.83	-0.515	"
Mercury Thiomalate $Hg(TS)_2$	" "	9.1	1.00	4.37	4.37	-0.52	"
" "	" "	9.1	0.50	2.225	4.45	-0.515	"
Thiomalic acid	$NaH_2PO_4 + Na_2HPO_4$	7.2	0.50	1.4875	2.975	-0.390	"
Mercury thiomalate $Hg(TS)_2$	" "	7.2	1.00	4.612	4.612	-0.398	"

TABLE II

$2 \times 10^{-3}M$ Thiomalic acid in ammonia buffer at pH 8.3

Height of the mercury column in cms.	Diffusion current (i_d) in μA	i_d/\sqrt{h}
50	6.517	0.922
45	6.267	0.934
40	5.817	0.920
35	5.517	0.933
30	5.017	0.916
25	4.617	0.923

TABLE III
 10^{-3} Thiomalic acid in Borax Buffer at pH 9.1

Height of the mercury in cms.	Diffusion current (i_d) in μA	i_d/\sqrt{h}
50	3.135	0.443
45	2.995	0.446
40	2.825	0.446
35	2.625	0.443
30	2.445	0.446

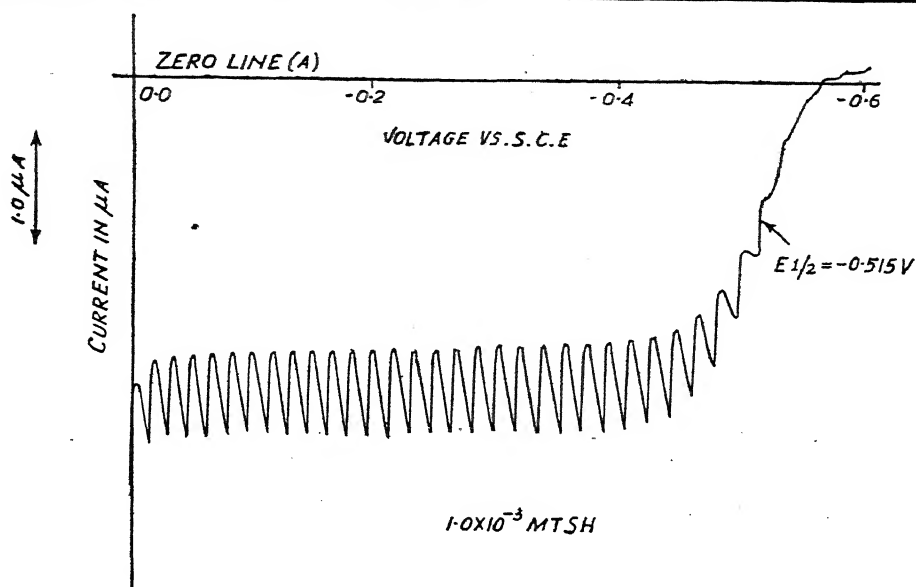


Fig. 1. Anodic wave of thiomalic acid in borax buffer (pH 9) (Uncorrected of residual current).

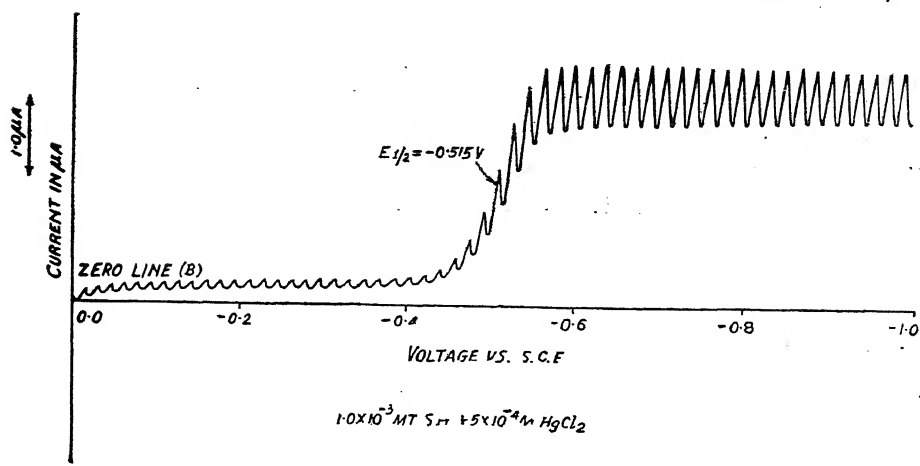


Fig. 2. Cathodic wave of the mercury-thiomalic acid compound (uncorrected for residual current).

Figure 3 shows a polarogram of a mixture of thiomalic acid and mercuric chloride $2 \times 10^{-3} + 5 \times 10^{-4} M$. A separate polarogram of a mixture of $10^{-3} M$ thiomalic acid and $5 \times 10^{-4} M$ mercuric chloride is also shown in figure 2.

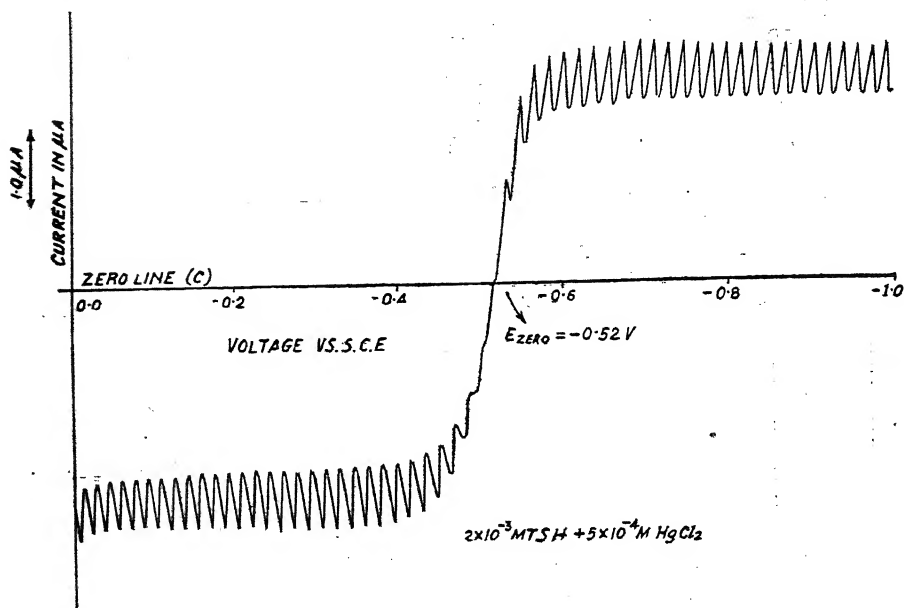


Fig. 3 Comparative anodic-cathodic wave of thiomalic acid and mercury-thiomalic acid compound (uncorrected for residual current).

In the latter case a purely cathodic wave is obtained whose E_1 is the same as the anodic wave of thiomalic acid.

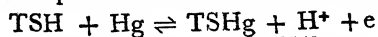
The polarogram in fig. 3 shows a composite wave containing cathodic and anodic currents. The zero current value is $-0.52v$ which is nearly the E_1 value of thiomalic acid and the cathodic wave of mercury compound. Polarograms obtained by the solution of the prepared mercuric compound are exactly similar to that in fig. 2.

DISCUSSION

The anodic wave of thiomalic acid is due to one electron change at the D. M. E. It cannot therefore be due to the oxidation of thiomalic acid to dithiomalic acid.



The anodic wave corresponds to the formation of the following:

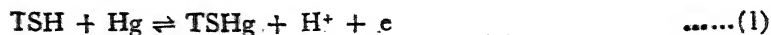


Stricks and Kolthoff have found a similar reaction with reduced glutathione⁸.

However the anodic wave is reversible and has the same half-wave potential as that of a compound of mercury with thiomalic acid ($\text{C}_8\text{H}_{10}\text{O}_8\text{S}_2\text{Hg}$)

Analysis of the cathodic wave of mercury compound gives a $\left(\frac{id-i}{i}\right)$ vs voltage)

slope of 0.0565v. This again corresponds to one electron change at the cathode. On the other hand the i_d/c value is 4.15 (compare 2.83 for thiomalic acid) taking the molecular formula as $C_5H_{10}O_3S_2$ Hg. The reaction can therefore be best represented by the following mechanism :



The second reaction is not observed at the electrode, but can explain the path taken by the mercuric compound to undergo a one electron reduction.

ACKNOWLEDGMENTS

The investigation was supported by a research grant from the U. P. Govt. Scientific Research Committee. One of the authors (S. K. T.) wishes to acknowledge the award of a research scholarship from the same committee.

The authors wish to thank Evans Chemetics Inc., New York (U. S. A.) for supplying thiomalic acid free of charge.

REFERENCES

1. Kapoor, R. C. and Tiwari, S. K., *Proc. Natl. Acad. Sci. (India)* **28A**, 52 (1959)
2. Taimni, I. K., and Salaria, G. B. S., *Analyt. Chim. Acta*, **12**, 519 (1955)
3. Stricks, W. and Kolthoff, I. M., *J. Amer. Chem. Soc.*, **74**, 4646 (1952)

POLAROGRAPHY OF THIOMALIC ACID (PART III)

(Investigations in acidic media)

By

S. K. TIWARI and R. C. KAPOOR

Chemical Laboratories, University of Allahabad, Allahabad

[Received on 12th October 1959]

ABSTRACT

Polarography of thiomalic acid has been studied in continuation with the previously reported studies in neutral and alkaline media.

The results confirm the previous findings, that the anodic wave is due to the formation of a mercury thiomalic acid compound. The reaction at the electrode is reversible and is due to one electron change.

The results obtained in the alkaline and neutral media have been compared and diffusion constants of thiomalic acid have been reported at different hydrogen ion concentrations.

Polarographic behavior of thiomalic acid has been further studied in acidic media. The findings are in continuation with those reported earlier (1), (2).

Acetate buffer (pH 5), citrate buffer (pH 5) and perchloric acid (pH 1) have been used as the supporting media. The anodic current given by the depolarization of electrode by thiomalic acid has been studied. The mercury compound of the acid has also been investigated.

MATERIALS

All the materials used were the same as reported earlier (2). The preparation of the mercury compound and its analysis has been described earlier. The chemicals used were Analar grade.

EXPERIMENTAL

The details of the determination of current-voltage curves have been given earlier (2). The characteristics of the capillary are:

$m = 1.376 \text{ mg. sec}^{-1}$; $t = 5.5 \text{ sec.}$ (open circuit); $m^{2/3} t^{1/6} = 1.644 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$; $h = 40 \text{ cms.}$

RESULTS AND DISCUSSIONS

Polarograms have been obtained in acetate buffer, citrate buffer and perchloric acid media. The reaction again is diffusion controlled as can be seen from table 2. The plots of $\log (i_a - i)/i$ vs voltage give slopes of 0.054 in acetate buffer (pH 5) and 0.0598 in perchloric acid buffer (pH 1.3). The values agree fairly well with the theoretical value for one electron change at the electrode.

Table I contains observations for thiomalic acid and also mercury-thiomalic acid compound. The nature of the anodic wave is similar to those obtained at pH 9 and pH 7. The table III includes the values of diffusion constants in different media. Table IV give E_3 values of thiomalic acid at different pH values. The values obtained at pH 7 and pH 9 are also included. A plot of E_3 against the pH gives a slope of 0.0585v for a unit change of pH.

TABLE I
Polarograms of thiomalic acid in acidic media at 30°C.

Compound	Buffer	pH	Concentration $M \times 10^3$ (c)	Diffusion current (i_d) in μA	i_d/c	E_1
Thiomalic acid	$CH_3COOH + CH_3COONa$	4.7	0.952	2.49	2.62	-0.255
" "	" "	"	1.36	3.56	2.62	-0.26
" "	" "	"	1.73	4.527	2.62	-0.26
" "	" "	"	2.08	5.493	2.64	-0.265
Mercury thio- malate $Hg(TS)_2$	" "	4.85	1.00	4.820	4.82	-0.272
Thiomalic acid	Citric acid + Na_2HPO_4	4.8	0.95	2.423	2.55	-0.26
" "	" "	"	1.36	3.54	2.60	-0.265
" "	" "	"	1.73	4.457	2.58	-0.265
" "	" "	"	2.08	5.324	2.56	-0.265
" "	$HClO_4$	1.4	0.50	1.450	2.90	-0.05
" "	" "	"	0.952	2.775	2.91	-0.055
" "	" "	"	1.36	4.015	2.95	-0.055
" "	" "	"	1.73	5.075	2.93	-0.055
" "	" "	"	2.08	6.225	2.99	-0.065
Mercury thio- malate $Hg(TS)_2$	" "	"	0.666	4.00	6.00	-0.05

TABLE II
 $5 \times 10^{-4}M$ Thiomalic acid in perchloric acid buffer at pH 1.1

Height of the mercury column in cms. (h)	Diffusion current (i_d) in μA	i_d/\sqrt{h}
55	1.60	0.215
50	1.51	0.213
45	1.42	0.211
40	1.33	0.210
35	1.29	0.218
30	1.20	0.219

TABLE III

Calculated values of diffusion constant (D) by Ilkovic equation.

Buffer	pH	Diffusion Constant $\times 10^6$
Borax + KCl	9.1	8.01
NH ₄ Cl + NH ₄ OH	8.8	7.35
NaH ₂ PO ₄ + Na ₂ HPO ₄	7.2	8.88
CH ₃ COOH + CH ₃ COONa	4.7	6.88
Citrate + Na ₂ HPO ₄	4.8	6.66
HClO ₄	1.4	8.64

TABLE IV

Half wave potentials (E_2) in different media.

Buffers	pH	E_2 in volts
Borax + KCl	9.1	-0.515
NH ₄ Cl + NH ₄ OH	8.8	-0.520
NaH ₂ PO ₄ + Na ₂ HPO ₄	7.2	-0.390
CH ₃ COOH + CH ₃ COONa	4.7	-0.26
Citrate + Na ₂ HPO ₄	4.8	-0.265
HClO ₄	1.4	-0.055

The results obtained confirm the findings given in the previous paper. The anodic wave at the electrode in acidic media is also due to the reaction between mercury and thiomalic acid. The varying dissociation of the H⁺ ions in different pH values does not seem to make any difference in the mercury thiomalic reaction.

There seems to be a small specific buffer action at pH 5.

ACKNOWLEDGEMENTS

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The authors wish to thank Evans Chemetics Inc., New York (U. S. A.) for supplying thiomalic acid free of charge.

REFERENCES

1. Kapoor, R. C. and Tiwari, S. K., *Proc. Natl. Acad. Sci. (India)*, **28A**, 52 (1959)
2. Tiwari, S. K. and Kapoor, R. C., *Proc. Natl. Acad. Sci. (India)* **28A**, 272 (1959)

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